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SECTION A

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No. 6—December, 1938.

Heterocyclic Compounds. Part IX. Coumarins from Substituted Resacetophenones and Ethyl Aceto-acetate	R. D. DESAI AND M. EKKELAS	567
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ERRATA*

RAMAN SPECTRA OF TERPENES

By W. ROGIE ANGUS

(Vol VIII, No 5, Section A, pp 529 to 565, of *Proc Ind Acad Sci*)

p 534, last line	For " Δ^1 α m Menthadlene"	read " Δ^1 α m Menthadlene"
p 537, line 13	Insert "ring"	after "cyclobutane"
p 538, last line	Insert " , "	after "standpoint"

Table I, pp 544-545

Geramol	Insert "1338(2)"	
Citronellol (56)	For "1295(f)"	read "1295(f)"
α Citral	Delete "298(2)"	
Citronellal (8)	Insert "298(2)" and "433(2)"	

Table II, pp 546-547

Limonene (7)	For "(409)(1)"	read "(490)(1)"
Δ^2 -m Menthe	For "22(f)"	read "222(f)"
Δ^1 -p-Menthe (23)	For "784(an3)" 799	read "784 } (an3)" 799 }
Δ^1 p Menthe (50)	For "834(m)"	read "864(m)"

Table II, pp 548-549

Limonene (43)	Insert "1043(2b)"	
Δ^2 m Menthe	Insert "1038(f)"	
Δ^1 p Menthe (50)	For "1313(aF)" 1374(aF) }	read "1313(aF)" "1374(aF)"
	For "1429(F)" 1462(m)"	read "1429(F)" 1462(m) }

Table III, pp 550-551

α -Terpineol (54)	Below "546($\frac{1}{2}$)"	insert "568($\frac{1}{2}$ d)"
Iso-Pulegyl Formate	For "237(f1)"	read "237(f 2)"
	For "925(1)"	read "925(f 1)"
	For "939(1)"	read "939(f1)"
Carvomenthol	For "512(f 2)"	read "513(f 2)"
Footnote, p 550 & p 552	For "a and b terpinols"	read "a and β terpinols"

* These corrections have been sent in by the author to whom, unfortunately, the proofs of the paper as originally printed could not be sent owing to the necessity for its speedy publication

Table III, pp 552-553

α Terpineol (54)	For " 2961(3) "	read " 2960(3) "
α Terpineol (4)	For " 1201 1315 } (B5) "	read " 1301 1315 } (B4) "
	For " 1412 1452 } (B 8) "	read " 1432 1452 } (B 8) "
	1467	1467
α Terpineol (47)	For " 1078 1145 } (3 sb) "	read " 1078(2) " " 1145(3sb) "
Isopulegol	For " 1235(an 4) "	read " 1235(an 5) "
Menthol	For " 1000(f 4) "	read " 1000(f 1) "
1 8 Cineol	For " 1100(6) "	read " 1100(3) "

Table IV, pp 554-555

Camphor (4)	Insert " 175(f2) "	
	For " 403(f1) "	read " 403(f2) "
Carvone (19)	For " 531(f1) "	read " 531(f2) "
	For " 628(f1) "	read " 638(f1) "
Carvotanacetone	For " 538(f1) "	read " 536(f1) "
Carvenone	For " 679 (1) "	read " 679(2) "
	Delete " 2961(3) "	

Table I, p 556

Sabinene (54)	For " 634(1) "	read " 634(3d) "
	For " 11214(1d) "	read " 1214(1d) "
β Thujone (19)	For " 325(f9) "	read " 625(f9) "
	For 1446 1471(f13) "	read " 1446 1471 } (f13) "

Table VI, p 557

Δ^3 Carene (27) Fr 19	For " 20(an3) "	read " 820(an3) "
Δ^4 Carene	For " 1397(2) "	read " 1379(2) "

Table VII (A), pp 558-559

α Pinene (11)	Insert " 994($\frac{1}{2}$) "	
α Pinene (5)	For " 2921 "	read " 2931 "
α Pinene (27)	For " 304(ab2) "	read " 304(an2) "
α Pinene (57)	For " 1381 "	read " 1381(2) "
α Pinene(65)	For " 620(1) "	read " (620)(1) "
	Insert " 606(4) "	
	For " 949(0) "	read " 949(3) "
	For " 2918(6b) "	read " 2917(6b) "
β Pinene (43)	For " 918 923(2b) "	read " 918 923 } (2b) "
	For " 949(2b) "	read " 949(1b) "

Table VII (B), pp 560-561

Myrtenol	For " 1451(an10) "	read " 1451(an12) "
Myrtanol	For " 857(an3) "	read " 857(an8) "
	For " 938 "	read " 937 "
Iso Myrtanyl Acetate	For " 861(f3) 878 "	read " 861 878 } (f3) "
Myrtenal	Insert " 840(n6) " and " 1263(n3) "	
Verbenone (31)	For " 117(B4) 134 "	read " 117 134 } (B4) "
Myrtenilidene Acetone	For " 142(B2) 161 "	read " 142 161 } (B2) "
	For " 1248 1216 } (B175) "	read " 1248 1267 } (B15) "

Table VIII, pp 562-563

Iso Bornyl Formate	For " 947(B5) 971 "	read " 947 971 } (B5) "
	For " 1170(B8) 1223 "	read " 1170 1223 } (B8) "
	For " 1243(B4) " 1260	read " 1243 1260 } (B4) "
Iso Bornyl Acetate	Insert " 368(f1) "	
	For " 1238(B2) 1258 "	read " 1238 1258 } (B2) "
Iso Bornyl Propionate	For " 1249(f) "	read " 1249(f3) "
Bornyl Butyrate	For " 1221 1232 } (B3) "	read " 1221 1232 } (B2) "
Iso-Bornyl Butyrate	For " 893(B1) ' 923	read " 893 923 } (B1) "
Camphenilone	For " 504(f1) "	read " 534(f1) "
Camphor (12)	For " 139(1) "	read " 169(1) "
Camphor (19)	Insert " 1020(f1) "	

Table VIII, pp 564-565

Camphor (64)	For " 2838(3) "	read " 2808(3) "
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HETEROCYCLIC COMPOUNDS.

Part VII. Coumarins from Resacetophenone and Cyclic- β -ketonic Esters.

BY NAZIR AHMAD CHOWDHRY

AND

R D DESAI

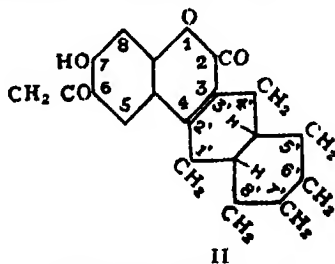
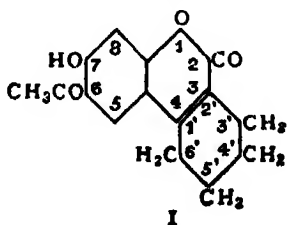
(From the Department of Chemistry, Muslim University, Aligarh)

Received May 6, 1938

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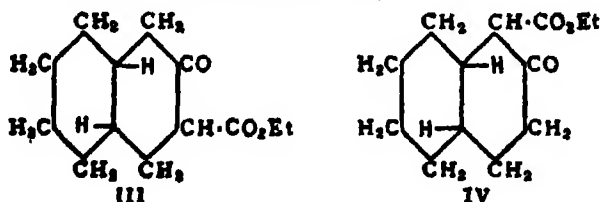
(Communicated by Dr R K Asundi, M Sc, PhD)

DESAI AND HAMID¹ showed that resacetophenone condensed with acetoacetic ester in the presence of phosphorus oxychloride with the formation of 7-hydroxy-6-acetyl-4-methylcoumarin. Extending this reaction to ethylcyclohexanone-2-carboxylate, we find that resacetophenone under similar conditions, gives 7-hydroxy-6-acetyl-(1' 2' 4 3)-cyclohexenocoumarin (I). Its constitution was established by the fact that it gave a strong ferric chloride reaction showing the *ortho*-position of OH and -COCH_3 groups. Further, reduction by Clemmensen's method gave 7-hydroxy-6-ethyl-(1' 2' 4 3)-cyclohexenocoumarin which was also prepared for comparison by condensing 4-ethyl-resorcinol with cyclohexanone-2-carboxylate in the presence of concentrated sulphuric acid.



Other cyclic- β -ketonic esters like 4-methylcyclohexanone-2-carboxylate, 5-methylcyclohexanone-2-carboxylate and *trans*- β -decalone-3-carboxylate condensed similarly with resacetophenone with the formation of 7-hydroxy-6-acetyl-4'-methylcyclohexeno-(1' 2' 4 3), 7-hydroxy-6-acetyl-5'-methylcyclohexeno-(1' 2' 4 3)-, and 7-hydroxy-6-acetyl-*trans*-octalino-(2' 3' 4 3)-coumarins (II). As each of them was reducible by zinc amalgam to their 7-hydroxy-6-ethyl analogues which could be easily prepared from 4-ethyl-resorcinol and the respective β -ketonic esters, the constitution of these coumarins was clearly established.

Ethyl-2-keto-*trans*-decalin-3-carboxylate was prepared by the application of Kotz's² method, according to Huckel and Goth,³ but the latter investigators have not determined the constitution. We found that oxidation with alkaline potassium permanganate gave a quantitative yield of *trans*-cyclohexane-1,2-diacetic acid, which could arise only from 3-carboxylate (III) and not from 1-carboxylate (IV)



6-Methylcyclohexanone-2-carboxylate did not react with resacetophenone in the presence of phosphorus oxychloride. We are busy condensing these esters with substituted resacetophenones as well as the preparation of coumarino-chromones from these coumarins.

Experimental

7-Hydroxy-6-acetyl-cyclohexeno-(1' 2' 4 3)-coumarin—A mixture of cyclohexanone-2-carboxylate (5 g), resacetophenone (4.5 g), phosphorus oxychloride (3 c.c.) and dry benzene (25 c.c.) was heated on the water-bath under reflux for three hours. The benzene solution was poured off, and the sticky, black residue was thrice extracted with benzene (15 c.c., each lot). The residue left after the removal of benzene crystallised from dilute alcohol in needles, m.p. 237° C. (Found C, 69.5, H, 5.5, $C_{15}H_{14}O_4$ requires C, 69.8, H, 5.4 per cent.) The coumarin is soluble in alcohol, acetone, benzene and glacial acetic acid but sparingly soluble in hexane and petrol. Its alcoholic solution gives a reddish-violet colouration with ferric chloride.

The *acetyl derivative* prepared by heating the coumarin (0.5 g) with acetic anhydride (5 c.c.) on a sand-bath for three hours, crystallised from dilute alcohol in needles melting at 199° C. (Found C, 67.9, H, 5.4, $C_{17}H_{16}O_5$ requires C, 68.0, H, 5.3 per cent.)

Reduction to 7-hydroxy-6-ethyl-cyclohexeno-(1' 2' 4 3)-coumarin.—An alcoholic solution of the above coumarin (0.5 g) was added to amalgamated zinc dust (5 g) covered with hydrochloric acid (15 c.c.) and the mixture was heated under reflux on sand-bath for three hours. The precipitate obtained on cooling was filtered off, extracted with alcohol to get rid of zinc dust and the alcoholic solution concentrated, when prismatic needles melting at 218°C. were obtained. This was identical in m.p. and mixed m.p. with the

coumarin obtained from 4-ethylresorcinol and cyclohexanone-2-carboxylate, by Z. Ahmad and Desai ⁴

7-Hydroxy-6-acetyl-4'-methylcyclohexeno-(1' 2' 4 3)-coumarin, was similarly prepared from resacetophenone (5 g), 4-methylcyclohexanone-2-carboxylate (5 g), POCl₃ (3 c c), and dry benzene (20 c c) as usual, and crystallised from dilute alcohol in fine needles melting at 262° C. Its alcoholic solution gave a reddish-brown colour with ferric chloride (Found C, 70.4, H, 5.8, C₁₈H₁₆O₄ requires, C, 70.6, H, 5.9 per cent). Reduction with amalgamated zinc dust gave *7-hydroxy-6-ethyl-4'-methylcyclohexeno-(1' 2' 4 3)-coumarin*, identified by m p and mixed m p with an authentic specimen.

A mixture of 4-ethylresorcinol (3 g), 4-methylcyclohexanone-2-carboxylate (3 g) and concentrated sulphuric acid (10 c c) was left overnight and poured over ice. The solid crystallised from dilute alcohol in tiny plates melting at 252° C. It dissolved in alkali with a yellow colour and blue fluorescence. (Found C, 74.1, H, 7.1, C₁₈H₁₈O₃ requires C, 74.4, H, 7.0 per cent). The *acetyl derivative* crystallised from dilute alcohol in lustrous plates melting at 146° C (Found C, 72.1, H, 6.8, C₁₈H₂₀O₄ requires C, 72.0, H, 6.7 per cent). The *methyl ether* prepared by shaking the alkaline solution of the coumarin with dimethyl sulphate crystallised from dilute alcohol in flat needles melting at 158° C (Found C, 74.8, H, 7.6, C₁₇H₂₀O₃ requires C, 75.0, H, 7.6 per cent).

7-Hydroxy-6-acetyl-5-methylcyclohexeno-(1' 2' 4 3)-coumarin, was prepared from resacetophenone (3 g), 5-methylcyclohexanone-2-carboxylate (3 g), POCl₃ (3 c c) and dry benzene (20 c c) by the usual method and crystallised from dilute alcohol in small needles melting at 258° C. Its alcoholic solution gave a reddish colour with ferric chloride (Found C, 70.6, H, 6.0, C₁₈H₁₆O₄ requires C, 70.6, H, 5.9 per cent). It could be reduced to *7-hydroxy-6-ethyl-5'-methylcyclohexeno-(1' 2' 4 3)-coumarin*, identified by m p and mixed m p with an authentic specimen.

7-Hydroxy-6-ethyl-5'-methylcyclohexeno-(1' 2' 4 3)-coumarin, was obtained by the usual method from 4-ethylresorcinol and 5-methylcyclohexanone-2-carboxylate and crystallised from dilute alcohol in small plates melting at 202° C. The yellowish alkaline solution gave blue fluorescence, while its solution in concentrated sulphuric acid gave violet fluorescence (Found: C, 74.2, H, 6.9, C₁₈H₁₈O₃ requires C, 74.4, H, 7.0 per cent). The *acetyl derivative* crystallised from dilute alcohol in fine needles melting at 167° C (Found: C, 71.8, H, 6.9, C₁₈H₂₀O₄ requires C, 72.0; H, 6.7 per cent.). The *methyl ether* crystallised from alcohol in lustrous plates

melting at 127° C (Found C, 74.9, H, 7.7, $C_{17}H_{20}O_3$ requires C, 75.0, H, 7.6 per cent)

Preparation of trans-β-decalone-3-carboxylate—This was prepared by a slight modification of the method of Huckel and Goth (*loc cit*)

To a cooled solution of sodium ethoxide (6.6 g Na, 80 c.c. absolute alcohol) a mixture of *trans*-β-decalone (42 g) and absolute ethyl oxalate (42 g) was slowly added with constant shaking, and the mixture allowed to stand in ice-cold water for six hours and then at the ordinary temperature for four days. The mixture was freely diluted with water, and made slightly acidic with ice-cold hydrochloric acid, when a thick oil was precipitated. This was extracted with ether, and the ethereal solution was extracted with 5 per cent NaOH solution to remove the unreacted decalone. The alkaline solution on acidification gave almost pure *trans*-β-decalone-3-glyoxalate which was extracted with ether, dried and recovered. Its alcoholic solution gave a blood-red coloration with ferric chloride. It was heated in an oil-bath at 180° C for two hours, taken up in ether, and the ethereal solution extracted with 5 per cent NaOH solution to remove β-decalone which was also formed as a by-product during heating. The alkaline solution on acidification, gave *trans*-β-decalone-3-carboxylate which was extracted with ether, dried and distilled. It boiled at 145–50° C /6 mm, and immediately solidified on cooling to large, beautiful, rectangular plates, melting at 46° C. It could be easily crystallised from hexane. Its alcoholic solution gave indigo-blue colour with ferric chloride.

Oxidation to trans-cyclohexane-1,2-diacetic acid—To the ester (0.5 g) dissolved in N/10 NaOH (20 c.c.) 5 per cent potassium permanganate (40 c.c.) was gradually added, and thoroughly shaken. Sulphur dioxide was passed to remove the excess of permanganate and the precipitated manganese dioxide was filtered off. The alkaline solution was concentrated on the sand-bath, and strongly acidified with concentrated hydrochloric acid, when a crystalline acid melting at 164° C was obtained. This was identified as *trans*-cyclohexane-1,2-diacetic acid by mixed melting point with an authentic specimen obtained by oxidising *trans*-β-decalone with concentrated nitric acid according to the instructions of Kandiah.⁵

7-Hydroxy-6-acetyl-trans-octalino-(2' : 3' . 4 . 3)-coumarin, was prepared by the usual method from resacetophenone (3 g), *trans*-β-decalone-3-carboxylate (3 g), POCl₃ (2 c.c.) and dry benzene (15 c.c.). The coumarin crystallised from dilute alcohol in fine needles melting at 250° C. Its alcoholic solution gave brownish-red coloration with ferric chloride (Found C, 73.0; H, 6.5; $C_{18}H_{16}O_4$ requires C, 73.1; H, 6.4 per cent). When reduced

by amalgamated zinc, it gave 7-hydroxy-6-ethyl-trans-octalino-(2' 3' . 4 3)-coumarin, which was also obtained by condensing 4-ethylresorcinol (3 g) with *trans*- β -decalone-3-carboxylate (4.4 g) in presence of concentrated sulphuric acid (15 c.c.) It crystallised from dilute alcohol in needles melting at 308° C. This coumarin forms a sparingly soluble sodium salt when treated with a dilute solution of caustic soda, and gives blue fluorescence. It could not be methylated by alkali and dimethyl sulphate (Found C, 76.2, H, 7.3, $C_{18}H_{22}O_3$ requires C, 76.5, H, 7.4 per cent)

The *acetyl derivative* crystallised from dilute alcohol in needles melting at 172° C (Found C, 73.9, H, 7.2, $C_{21}H_{24}O_4$ requires C, 74.1, H, 7.0 per cent)

Summary

Resacetophenone has been condensed with cyclic- β -ketonic esters like cyclohexanone-2-carboxylate, alkylcyclohexanone-2-carboxylates and *trans*- β -decalone-3-carboxylate in the presence of phosphorus oxychloride with the formation of 7-hydroxy-6-acetyl derivatives of cyclohexeno- and octalino-coumarins

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DIFFRACTION OF LIGHT BY SUPERPOSED ULTRASONIC WAVES.

BY M A GOVINDA RAU

Received July 11, 1938

IN his recent book on *Der Ultraschall*, L. Bergmann has reproduced some striking pictures of the diffraction effects observed when a beam of light traverses normally an ultrasonic sound field produced by a quartz crystal immersed in a liquid and simultaneously excited at two of its harmonics. If $k_1 n$ and $k_2 n$ are the two harmonics, then beside the diffraction lines due to $k_1 n$ and $k_2 n$, combinational lines due to $k_1 n \pm k_2 n$ also appear. A reference to the original paper¹ (1934) showed that he had also obtained similar combinational lines with crystals of different thicknesses, simultaneously excited at two incommensurate frequencies. Early this year, in January, it was thought that a natural explanation for this phenomenon could be provided by the simple theory of Raman and Nath.² Actually Mr. Nagendra Nath in a private communication to Prof. Sir C. V. Raman, had indicated that according to the theory, the consequence of such a superposition of two wave systems would be to give rise to the appearance of new combinational lines, whose number and intensity will vary much with the intensity of either of the original lines. Thus new lines corresponding to $m_1 \pm sn_2$ will occur, the intensity being given by the expression

$$J_r^2(v_1) J_s^2(v_2),$$

where $J_r(v_1)$ is a Bessel function of the r th order, and $v_1 = \frac{2\pi \mu_1 L}{\lambda}$, μ_1 being the maximum change in refractive index in the liquid, L the length of the light path in the sound field, and λ the wave length of light.

In order to verify these conclusions, it was thought worthwhile to repeat Bergmann's experiments more systematically, and with different sets of frequencies and intensities. The work had been partly completed when another paper by L. Bergmann³ (1938) appeared, in which besides some of our observations, further extensions of same to diffraction by sound waves set up in glass, have been beautifully recorded. However, we publish herewith some of our pictures, illustrating the effects of varying intensities clearly. In Fig. 1, two different intensities of the first order in (a) were obtained by slight obliquity of incidence, and similarly also for the

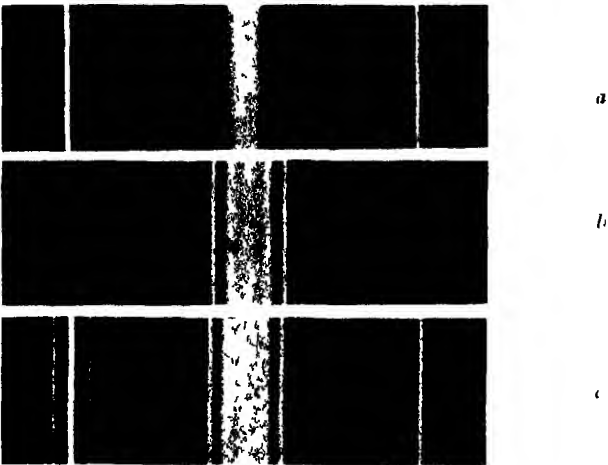


FIG 1

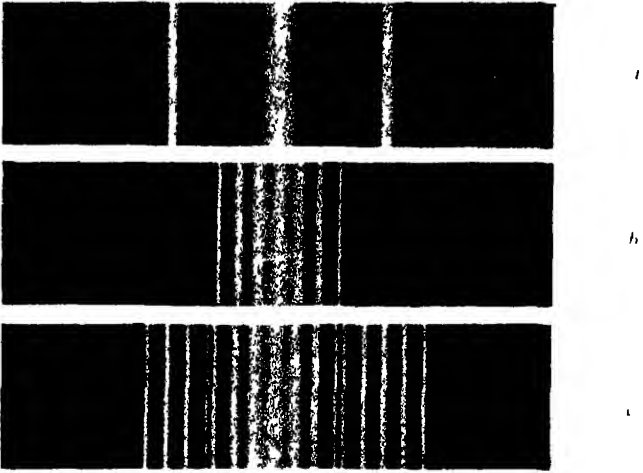


FIG 2

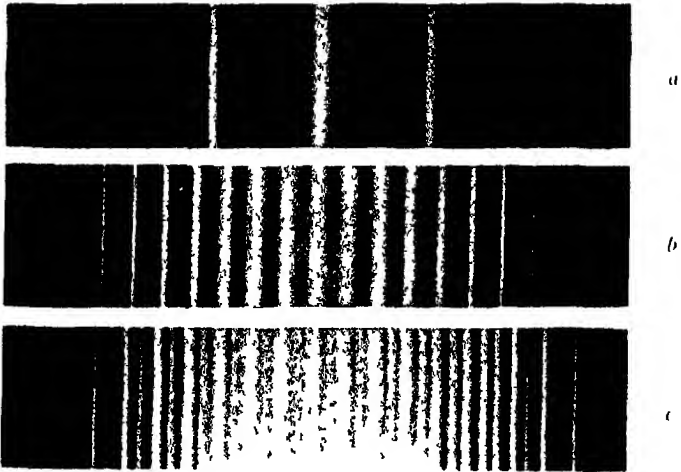


FIG 3

second orders in Fig 2 (a) As is clear from the pictures in Fig 1, the combination lines come out considerably brighter about the stronger first order on the left Similarly in Fig 2 (c), the larger number of combinational lines on the right are due to the additional lines arising out of the second order line Fig 3 is reproduced just to illustrate further the large number of combinational lines made visible, when one of the spectra (b) is strongly developed combinations such as $n_2 \pm 8n_1$, $2n_2 \pm 5n_1$ can be identified in the picture

The experiments were all carried out in the usual manner, but with two different crystals excited by separate oscillators, and immersed in xylol vertically at the opposite ends of a square glass trough

Some theoretical aspects of these combination lines have also been worked out here by Mr K N Rao, but they will not be reproduced here in view of the recent publications of the full papers by Nagendra Nath⁴ and also by E Feus³

The author takes great pleasure in expressing in this connection his gratitude to Prof Sir C V Raman, at whose suggestion this work was taken up before Bergmann's second paper appeared

Summary

Pictures are reproduced of the diffraction patterns obtained with light that has traversed a system of superposed ultrasonic waves set up in a liquid Besides the presence of the combinational lines, the pictures clearly show the characteristic manner in which their number and intensities depend upon the intensity of the original spectral orders

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AN APPLICATION OF THE BI-PARTITIONAL FUNCTION $H_g(P, Q)$ IN THE ENUMERATION OF DIFFERENT SAMPLES FROM FINITE POPULATION.

BY P V SUKHATME, B SC., PH D

(Statistician, Imperial Institute of Sugar Technology, Cawnpore.)

Received June 22, 1938

(Communicated by Prof P C Mahalanobis, I K S)

THE bi-partitional function $H_g(P, Q)$ is defined as

$$h_{p_1} h_{p_2} \cdots h_{p_p} = \sum H_g(P, Q) g(q_1 q_2 \cdots q_\sigma) \quad (1)$$

where P and Q stand for the partitions $(p_1 p_2 \cdots p_p)$ and $(q_1 q_2 \cdots q_\sigma)$ respectively of the same partible number $\omega (= \sum p_i = \sum q_i)$, $g(q_1 q_2 \cdots q_\sigma)$ is a monomial symmetric function of the quantities $x_1 x_2 \cdots$ given by

$$g(q_1 q_2 \cdots q_\sigma) = \sum (x_1^{q_1} x_2^{q_2} \cdots x_\sigma^{q_\sigma}), \quad (2)$$

the h -function of the p th degree called the homogeneous product sum is given by

$$h_p = \sum g(p) \quad (3)$$

the summation being taken over all the monomial symmetric functions represented by the partitions of the number p , and the summation \sum in equation (1) is taken over all partitions Q of the weight ω . The properties of this bi-partitional function, its connection with distributions *in plano* and with the combinatorial problem of which it affords solution and the arithmetical method of evaluating it for large partitions are described in detail in a recent paper by the author in the *Phil Trans*¹. The practical method of its evaluation put forth in the above paper is primarily due to R A Fisher. It is proposed in this note to exhibit its application in the enumeration of different samples of given size drawn from a finite population.

We shall do well to recall the arithmetical method of evaluating $H_g(P, Q)$. We need consider the special case when either P or Q contains two parts only. Let $P = (p_1, p_2 \cdots p_p)$ and $Q = (q, \omega - q)$. For evaluating $H_g(P, Q)$, all the different partitions of q or $(\omega - q)$ whichever is less, having parts less than or equal to p are listed and the numbers of ways in which the parts of each of the different partitions of q or $(\omega - q)$ are obtained from the parts of P are recorded. The sum for all partitions represents $H_g(P, Q)$. Thus to evaluate $H_g(42^3, 53)$ The different partitions of 3 having parts less than or equal to $p - 3$, are recorded. These are (3), (21) and (1³). The

¹ P V. Sukhatme, *Phil. Trans. Roy Soc London, A*, No 780, Vol 237, 375-409

part 3 of the partition (3) may be obtained from the parts of (42²) in one way only, the parts 2, and 1, may be obtained in six ways from the parts of (42²) and finally the parts of (1³) may be obtained in one way only from the parts of (42²). The process is systematically carried out as follows

	(3)	(21)	(1 ³)	
(42 ²)	1	6	1	8

giving $Hg(P, Q) = 8$

A partition $(p_1 p_2 \dots p_p)$ may be interpreted to mean that of the $\omega = \sum p_i$ quantities comprising a finite population p_i quantities have a value 1 each, p_2 have a value 2 each and so on. Conversely a finite population of size ω can always be specified by a partition of the same weight ω .

The total number of ways in which samples of size q can be drawn from a population of size ω is $\frac{\omega!}{q!(\omega - q)!}$ and is obviously equal to the number of ways of drawing samples of size $(\omega - q)$ from a population of the same size. All the $\frac{\omega!}{q!(\omega - q)!}$ samples will not however be different in composition giving different moment-statistics. The number of different samples of size q which can be drawn from the population $(p_1 p_2 \dots p_p)$, will necessarily be represented by such partitions of the number q , which have the number of parts less than or equal to p and whose parts are chosen in all different ways from the parts of the partition $(p_1, p_2 \dots p_p)$. The arithmetical process described above clearly shows that the number of different samples of size q drawn from the population $(p_1 p_2 \dots p_p)$ of size ω is given by $Hg(P, Q)$; where $P = (p_1 p_2 \dots p_p)$ and $Q = (q, \omega - q)$ or *vice versa* since $Hg(P, Q) = Hg(Q, P)$.

To take an example, suppose we have a population represented by the partition (1, 6, 8, 12). The interpretation attached to this partition is that of the 27 quantities comprising this population, 1 has a value one, 6 have values two each, 12 have values three each and the remaining 8 have values 4 each. The population will be represented by means of a frequency distribution as follows.

Value of the variate	1	2	3	4
Frequency	1	6	12	8 = 27

The problem is to enumerate all the different samples of size, say 8, which can be drawn from this population. The necessary calculations are shown below —

Partitions of 8 of parts ≤ 4	No. of different samples	Specification 1 2 3 4	Frequency
(8)	2	. . 8 8	495 1
(71)	6	1 7 1 . 7 1 7 1 7 1 1 7 1 7 .	96 48 8 6336 4752 792
(62)	6	2 6 2 6 2 6 2 6 2 . 6 2	420 1848 13860 25872 66 28
(53)	6	5 3 . 5 . 3 3 5 . 5 3 3 5 . 3 5	1320 336 15840 44352 1120 12320
(4 ²)	3	. 4 4 . 4 4 . 4 . 4	7425 34650 1050
(61 ²)	9	1 6 1 . 1 6 . 1 1 6 1 1 1 1 6 . 1 . 6 1 . 1 6 1 1 1 6 1 . 1 6 . 1 1 6	12 8 96 5544 7392 44352 168 336 2016
(521)	12	1 2 5 1 2 . 5 1 . 2 5 1 5 2 1 5 2 1 5 2 1 . 5 2 . 1 5 2 . 1 2 5 . 2 5 1	11880 840 3696 396 168 22176 133056 22176 95040

Partitions of 8 of parts ≤ 4	No. of different samples	Specification 1 2 3 4	Frequency
(431)	12	2 1 5	10080
		. 5 1 2	2016
		. 5 2 1	3168
		1 4 3	3300
		1 3 4	9900
		1 4 3	27720
		1 3 4	15400
		1 4 3	840
		1 3 . 4	1400
		1 4 3	166320
		1 3 4	8400
		. 4 3 1	26400
		4 1 3	10080
		. 3 1 4	16800
		3 4 1	79200
(42 ²)	3	4 2 2	27720
		2 4 2	207900
		2 2 4	69300
(3 ² 2)	3	3 3 2	123200
		3 2 3	73920
		2 3 3	184800
(51 ²)	3	1 5 1 1	576
		1 1 5 1	38016
		1 1 1 5	4032
(421 ²)	6	1 4 2 1	7920
		1 4 1 2	5040
		1 2 4 1	59400
		1 2 1 4	12600
		1 1 4 2	83160
		1 1 2 4	27720
(32 ² 1)	3	1 3 2 2	36960
		1 2 3 2	92400
		1 2 2 3	55440
(3 ² 1 ²)	3	1 3 3 1	35200
		1 3 1 3	13440
		1 1 3 3	73920
TOTAL ..	77		$\left(\frac{27!}{8!19!} \right)$

It will be seen that the number of different samples is 77 which is equal to $Hg\{(1, 6, 12, 8), (8, 19)\} = Hg\{(8, 19), (1, 6, 12, 8)\}$.

HETEROCYCLIC COMPOUNDS.

Part VIII. Coumarins from Alkylcyclohexanone-2-carboxylates and *Trans*- β -decalone-3-carboxylate.

BY NAZIR AHMAD CHOWDHRY

AND

R D DESAI

(From the Department of Chemistry, Muslim University, Aligarh)

Received June 21, 1938

(Communicated by Dr R K Asundi, M Sc, PhD)

IN continuation of our work on the synthesis of coumarins from cyclic- β -ketonic esters,¹ we have now extended this investigation to the preparation of coumarins from 4-methyl-, 5-methyl-, and 6-methyl-cyclohexanone-2-carboxylates as well as *trans*- β -decalone-3-carboxylate by the Pechmann method. 5-Methylcyclohexanone-2-carboxylate has already been condensed with phloroglucinol, orcinol and pyrogallol in the presence of concentrated sulphuric acid, by Sen and Basu,² but we find that improved yields of the coumarins from these phenols are obtained by using phosphorus oxychloride, while concentrated sulphuric acid is the best condensing agent for resorcinol and α -naphthol.

Exactly identical results were obtained with 4-methyl-cyclohexanone-2-carboxylate and *trans*- β -decalone-3-carboxylate which condensed readily with the above phenols, but 6-methylcyclohexanone-2-carboxylate underwent coumarin condensation with all these phenols only in the presence of phosphorus oxychloride.

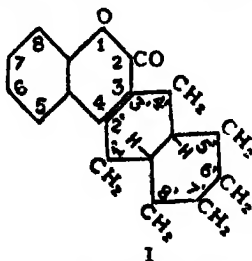
We have assumed the coumarin structure for all these products because of their unusual stability to the action of hot concentrated alkali. Sen and Basu (*loc cit*) have also observed the same stability in the case of their coumarins. If they had the alternative structure of substituted tetrahydro-xanthenes or cyclohexenochromones, they would have readily undergone fission to the alkylcyclohexanones and resorcylic acid as observed by Desai and Zafar-Uddin³ in the case of cyclopentenochromones.

Sen and Basu (*loc cit*) assumed that the coumarin obtained from orcinol and 5-methylcyclohexanone-2-carboxylate had the structure of 7-hydroxy-5-methyl-5'-methyl cyclohexeno-(1' 2' 4 3) coumarin but the absence of fluorescence and yellow colour of the alkali solution of these coumarins are against the 7-hydroxy structure. Therefore, we believe that this coumarin is 5-hydroxy-7-methyl-5'-methylcyclohexeno-(1' . 2' 4 3)-coumarin, and ~~the~~

same is the case with the other coumarins from orcinol. We have subjected the acetates of the coumarins from resorcinol and cyclic- β -ketonic esters to the Fries' Transformation in the presence of anhydrous aluminium chloride under the conditions used by Limaye⁴ in the case of 7-acetoxy-4-methylcoumarin, and find that the acetyl group migrates to the ring in the 8 position. The other possible position for migration is 6, but the coumarins having this constitution have already been synthesised by the authors (in the press) from resacetophenone and respective cyclic- β -ketonic esters, and are found to be quite different.

When the cyclic- β -ketonic esters are compared with their open-chain confreres like acetoacetic esters, it is found that the former are actually more reactive than the latter, so far as the coumarin formation is concerned, although the cyclic esters can be looked upon as monosubstituted acetoacetic esters where one of the hydrogens of the methylene group, and one of the hydrogens of the methyl group are replaced by $-\text{CH}_2\text{CH}_2-$ (in the case of cyclopentanone ester) and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ groups (in the case of cyclohexanone esters). This is possibly due to the highly enolic character of the cyclic- β -ketonic esters. The sluggishness of 6-methylcyclohexanone-2-carboxylate as compared with its 5-methyl- and 4-methyl-analogues can be attributed to the steric hindrance offered by the methyl group which is in the *ortho*-position to the enolic hydroxyl. Moreover, whereas the coumarins from dihydric and trihydric phenols obtained from 4-methyl and 5-methyl-cyclohexanone-2-carboxylates can be methylated by dimethyl sulphate and alkali, those obtained from 6-methylcyclohexanone-2-carboxylate cannot be methylated under this condition with the exception of the coumarin from resorcinol.

The nomenclature proposed in Part I of this series has been followed throughout, and in accordance with it, the coumarins from *trans*- β -decalone-3-carboxylate have been named *trans*-octalino-(2' 3' 4 3)-coumarin (I).



Experimental

(A) Coumarins from 4-methylcyclohexanone-2-carboxylate

7-Hydroxy-4'-methylcyclohexeno-(1' 2' 4 : 3)-coumarin —A cooled solution of resorcinol (2.5 g) and 4-methylcyclohexanone-2-carboxylate

(3.5 g) in concentrated sulphuric acid (16 c c) was left overnight at the ordinary temperature. The solid obtained by pouring the mixture over ice, crystallised from dilute alcohol in flat needles melting at 217°C . It dissolved in alkali with a slight yellow colour and blue fluorescence. Concentrated sulphuric acid dissolved it to a colourless solution giving violet fluorescence. (Found C, 72.8, H, 6.0, $\text{C}_{14}\text{H}_{14}\text{O}_2$ requires C, 73.0; H, 6.1 per cent.)

The *acetyl derivative* obtained by heating the coumarin (0.5 g) with acetic anhydride (5 c c) in presence of a few drops of pyridine for 4 hours, crystallised from alcohol in long needles melting at 176°C . (Found C, 70.4, H, 6.0, $\text{C}_{16}\text{H}_{16}\text{O}_4$ requires C, 70.6, H, 5.9 per cent.)

The *methyl ether* prepared by shaking the 5 per cent alkaline solution of the coumarin (0.5 g) with dimethyl sulphate (2 c c) crystallised from alcohol in long, fine needles melting at 123°C . (Found C, 73.5, H, 6.7; $\text{C}_{15}\text{H}_{16}\text{O}_2$ requires C, 73.8, H, 6.6 per cent.)

7-Hydroxy-8-acetyl-4'-methylcyclohexeno-(1' 2' 4 3)-coumarin—An intimate mixture of 7-acetoxy-4'-methylcyclohexeno-(1' 2' 4 3) coumarin (2 g) and anhydrous aluminium chloride (5 g) was heated in a round-bottom flask fitted with an air condenser at the temperature of 140°C for an hour. The cooled mixture was decomposed with ice-cold hydrochloric acid, and the resulting solid was purified through 5 per cent sodium carbonate solution. The solid obtained on the addition of concentrated hydrochloric acid crystallised from dilute alcohol in fine, silky needles melting at 135°C . Its alcoholic solution gave reddish-violet coloration with ferric chloride. (Found C, 70.3, H, 6.1, $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 70.6, H, 5.9 per cent.)

Its *semicarbazone* prepared by heating its alcoholic solution with semicarbazide acetate for 15 minutes, crystallised from alcohol in small plates, melting at 236°C . (Found C, 61.7, H, 5.9, $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_2$ requires C, 62.0; H, 5.8 per cent.)

7,8-Dihydroxy-4'-methylcyclohexeno-(1' 2' 4 3)-coumarin, was similarly obtained from pyrogallol (2.5 g.) and concentrated sulphuric acid (12 c.c.). It crystallised from dilute alcohol in small, colourless cubes melting at 256°C . Its alcoholic solution gave a deep green colour with ferric chloride. The alkaline solution showed a weak blue fluorescence, while the concentrated sulphuric acid solution was deep yellow. (Found C, 68.1, H, 5.9; $\text{C}_{14}\text{H}_{14}\text{O}_4$ requires C, 68.3, H, 5.7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in fine needles, melting at 179°C . (Found C, 65.5, H, 5.6; $\text{C}_{16}\text{H}_{16}\text{O}_4$ requires C, 65.5; H, 5.5 per cent.)

The *dimethyl ether* crystallised from dilute alcohol in pointed needles, melting at 154°C (Found. C, 69.9, H, 6.5, $\text{C}_{16}\text{H}_{18}\text{O}_4$ requires C, 70.0, H, 6.6 per cent)

4-Methylcyclohexeno-(1' . 2' 4 . 3)-1 2-*naphtha-pyrone* prepared from *o*-naphthol crystallised from rectified alcohol in flat needles melting at 198°C (Found : C, 81.5, H, 6.0; $\text{C}_{18}\text{H}_{16}\text{O}_4$ requires C, 81.8, H, 6.1 per cent)

5-Hydroxy-7-methyl-4'-methylcyclohexeno-(1' 2' 4 3)-*coumarin* —A mixture of orcinol (2 g), the ester (3 g), phosphorus oxychloride (1 c c) and dry benzene (10 c c) was heated on a water-bath for one hour under reflux. The residue after the removal of benzene was crystallised from dilute alcohol, when tiny white plates, melting at 250°C , were obtained. Its solution in dilute alkali was yellow, and non-fluorescent (Found C, 73.6, H, 6.4; $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 73.8, H, 6.6 per cent)

The *acetyl derivative* crystallised from dilute alcohol in long, fine needles melting at 185°C (Found C, 71.2, H, 6.4, $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3, H, 6.3 per cent)

The *methyl ether* crystallised from dilute alcohol in long, fine needles melting at 140°C . (Found C, 74.2, H, 7.2, $\text{C}_{18}\text{H}_{18}\text{O}_3$ requires C, 74.4, H, 7.0 per cent)

5 7-Dihydroxy-4'-methylcyclohexeno-(1' 2' 4 3)-*coumarin*, was similarly obtained from phloroglucinol (2.6 g), the ester (3.4 g) and POCl_3 (2 c c.) and crystallised from chloroform in plates melting at 265°C . Its alkaline solution was yellow and non-fluorescent (Found C, 68.2, H, 5.8, $\text{C}_{14}\text{H}_{14}\text{O}_4$ requires C, 68.3, H, 5.7 per cent)

The *diacetyl derivative* crystallised from dilute alcohol in long prisms melting at 128°C (Found C, 65.3, H, 5.5, $\text{C}_{18}\text{H}_{18}\text{O}_6$ requires C, 65.5, H, 5.5 per cent)

The *dimethyl ether* crystallised from dilute alcohol in tiny plates melting at 133°C . (Found C, 69.8, H, 6.4, $\text{C}_{16}\text{H}_{18}\text{O}_4$ requires C, 70.0, H, 6.6 per cent)

(B) *Coumarins from 5-methylcyclohexanone-2-carboxylate*

7-Hydroxy-5'-methylcyclohexeno-(1' . 2' 4 3)-*coumarin*, prepared from resorcinol, crystallised from dilute alcohol in fine, colourless needles melting at 202°C . Its solution in concentrated sulphuric acid gave a violet fluorescence. The alkaline solution was faint yellow and had a blue fluorescence (Found C, 72.7, H, 6.2, $\text{C}_{14}\text{H}_{14}\text{O}_4$ requires C, 73.0, H, 6.1 per cent.)

The *acetyl derivative* crystallised from dilute alcohol in colourless plates, melting at 136°C . (Found C, 70.3, H, 6.1; $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 70.6, H, 5.9 per cent)

The *methyl ether* crystallised from dilute alcohol in small needles melting at 118°C (Found C, 73.6, H, 6.8, $\text{C}_{15}\text{H}_{18}\text{O}_2$ requires C, 73.8, H, 6.6 per cent)

7-Hydroxy-8-acetyl-5'-methylcyclohexeno-(1' 2' 4 3)-coumarin, obtained by the Fries' Transformation of 7-acetoxy-5'-methyl cyclohexeno-(1' 2' 4 3)-coumarin in the usual way, crystallised from dilute alcohol in fine, silky needles melting at 142°C Its alcoholic solution gave reddish-violet coloration with ferric chloride (Found C, 70.4, H, 6.0, $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 70.6, H, 5.9 per cent)

The *semicarbazone* was a microcrystalline solid melting at 232°C

5'-Methylcyclohexeno-(1' 2' 4 3)-1 2-*a-naphtha-pyrone*, prepared from *a*-naphthol, crystallised from dilute alcohol in needles melting at 173°C (Found C, 81.7, H, 6.3, $\text{C}_{18}\text{H}_{18}\text{O}_2$ requires C, 81.8, H, 6.1 per cent)

7 8-Dihydroxy-5'-methylcyclohexeno-(1' 2' 4 3)-coumarin, obtained from pyrogallol, crystallised from dilute alcohol in tiny plates melting at 231°C Its solution in dilute alkali was yellow and fluorescent (blue) The alcoholic solution gave deep green colour with ferric chloride (Found C, 68.0, H, 5.8 Calc for $\text{C}_{14}\text{H}_{14}\text{O}_4$ C, 68.3, H, 5.7 per cent)

The *diacetyl derivative* crystallised from dilute alcohol in small needles melting at 214°C (Found C, 65.2, H, 5.7, $\text{C}_{18}\text{H}_{18}\text{O}_6$ requires C, 65.5, H, 5.5 per cent)

The *dimethyl ether* crystallised from hexane in needles melting at 123°C (Found C, 69.8, H, 6.6, $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 70.0, H, 6.6 per cent)

5-Hydroxy-7-methyl-5'-methylcyclohexeno-(1' 2' 4 3)-coumarin, prepared from orcinol, crystallised from dilute alcohol in colourless needles melting at 260°C [Sen and Basu (*loc. cit*) give 249°C] Its alkaline solution was yellow and non-fluorescent (Found C, 73.5, H, 6.8 Calc for $\text{C}_{18}\text{H}_{18}\text{O}_3$ C, 73.8, H, 6.6 per cent)

The *acetyl derivative* crystallised from dilute alcohol in fine needles melting at 134°C (Found C, 71.0, H, 6.2, $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3; H, 6.3 per cent)

The *methyl ether* crystallised from hexane in flat needles melting at 98°C (Found C, 74.1, H, 7.1; $\text{C}_{18}\text{H}_{18}\text{O}_2$ requires C, 74.4, H, 7.0 per cent)

5. 7-Dihydroxy-5'-methylcyclohexeno-(1' 2' 4 3)-coumarin, prepared from phloroglucinol crystallised from chloroform in tiny plates melting at 262°C . It dissolved in alkali with a yellow colour and no fluorescence. (Found: C, 68.0; H, 5.9. Calc for $\text{C}_{14}\text{H}_{14}\text{O}_4$. C, 68.3; H, 5.7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in small needles melting at 117° C (Found C, 65.4, H, 5.4, $C_{18}H_{18}O_6$ requires C, 65.5, H, 5.5 per cent)

(C) *Coumarins from 6-methylcyclohexanone-2-carboxylate*

This ester condenses with phenols in the presence of $POCl_3$ only

7-Hydroxy-6'-methylcyclohexeno-(1' 2' 4 3)-coumarin—A mixture of resorcinol (2.4 g), the ester (4.5 g), $POCl_3$ (2 c.c.), and dry benzene (10 c.c.) was heated under reflux on water-bath for two hours. Benzene was decanted off, and the residue was extracted with three lots of benzene (15 c.c. each time). The solvent was removed from the combined extracts, and the residue crystallised from alcohol in thick, lustrous plates melting at 205° C. The yellow alkaline solution showed a blue fluorescence while its solution in concentrated sulphuric acid was colourless but gave violet fluorescence (Found C, 72.7, H, 5.9, $C_{14}H_{14}O_3$ requires C, 73.0, H, 6.1 per cent)

The *acetyl derivative* crystallised from dilute alcohol in needles, melting at 174° C (Found C, 70.5, H, 6.1, $C_{16}H_{16}O_4$ requires C, 70.6, H, 5.9 per cent)

The *methyl ether* crystallised from alcohol in colourless needles, melting at 112° C (Found C, 73.6, H, 6.5, $C_{15}H_{16}O_3$ requires C, 73.8, H, 6.6 per cent)

7,8-Dihydroxy-6'-methylcyclohexeno-(1' 2' 4 3)-coumarin, obtained from pyrogallol, crystallised from alcohol in tiny plates melting at 227° C (Found C, 68.0; H, 5.8, $C_{14}H_{14}O_4$ requires C, 68.3, H, 5.7 per cent)

The *diacetyl derivative* crystallised from dilute alcohol in prisms melting at 140° C. (Found C, 65.2, H, 5.5, $C_{18}H_{18}O_6$ requires C, 65.5, H, 5.5 per cent)

5,7-Dihydroxy-6'-methylcyclohexeno-(1' 2' 4 3)-coumarin, obtained from phloroglucinol, crystallised from alcohol in small plates melting, at 275° C. (Found: C, 68.4, H, 5.7, $C_{14}H_{14}O_4$ requires C, 68.3, H, 5.7 per cent)

The *diacetyl derivative* crystallised from dilute alcohol in needles melting at 127° C. (Found: C, 65.4; H, 5.7, $C_{18}H_{18}O_6$ requires C, 65.5, H, 5.5 per cent.)

7-Hydroxy-6-ethyl-6'-methylcyclohexeno-(1':2' 4 3)-coumarin, obtained from 4-ethylresorcinol, crystallised from alcohol in rhombic needles, melting at 232° C. Its colourless solution in concentrated sulphuric acid gave violet fluorescence, while the yellow, alkaline solution gave blue fluorescence. (Found: C, 74.3; H, 7.2; $C_{20}H_{20}O_3$ requires C, 74.4, H, 7.0 per cent)

The *acetyl derivative* crystallised from alcohol in lustrous plates, melting at 118°C (Found C, 71.8, H, 6.9, $\text{C}_{18}\text{H}_{20}\text{O}_4$ requires C, 72.0, H, 6.7 per cent)

The *methyl ether* crystallised from dilute alcohol in long lustrous plates melting at 109°C (Found C, 74.7, H, 7.7, $\text{C}_{17}\text{H}_{20}\text{O}_3$ requires C, 75.0, H, 7.6 per cent)

5-Hydroxy-7-methyl-6'-methylcyclohexeno-(1' 2' 4 3)-coumarin, obtained from orcinol, crystallised from alcohol in tiny plates melting at 235°C . Its alkaline solution was yellow and devoid of fluorescence (Found C, 73.5, H, 6.7, $\text{C}_{18}\text{H}_{18}\text{O}_3$ requires C, 73.8, H, 6.6 per cent)

The *acetyl derivative* crystallised from alcohol in tiny needles, melting at 124°C (Found C, 71.0, H, 6.5, $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3, H, 6.3 per cent)

6'-Methylcyclohexeno-(1' 2' 4 3)-1 2- α -naphthapyrone, prepared from α -naphthol, crystallised from dilute alcohol in long needles melting at 112°C (Found C, 81.6, H, 6.2, $\text{C}_{18}\text{H}_{16}\text{O}_2$ requires C, 81.8, H, 6.1 per cent)

(D) *Coumarins from trans- β -decalone-3-carboxylate*

7-Hydroxy-trans-octalino-(2' 3' 4 3)-coumarin, prepared from resorcinol and the ester, crystallised from rectified spirit in pale-brown plates melting at 245°C . Its yellow, alkaline solution gave blue fluorescence. The colourless solution in concentrated sulphuric acid gave violet fluorescence. Ferric chloride gave green colouration to its alcoholic solution (Found C, 75.4, H, 6.8, $\text{C}_{17}\text{H}_{18}\text{O}_3$ requires C, 75.4, H, 6.7 per cent)

The *acetyl derivative* crystallised from alcohol in fine colourless needles, melting at 192°C (Found C, 72.8, H, 6.6, $\text{C}_{19}\text{H}_{20}\text{O}_4$ requires C, 73.1, H, 6.4 per cent)

The *methyl ether* crystallised from alcohol in colourless plates melting at 178°C (Found C, 75.9, H, 7.1, $\text{C}_{18}\text{H}_{20}\text{O}_3$ requires C, 76.1, H, 7.0 per cent)

7-Hydroxy-8-acetyl-trans-octalino-(2' 3' 4 3)-coumarin, was prepared by the Fries' Transformation of 7-acetoxy-trans-octalino-(2' 3' 4 3)-coumarin, and crystallised from alcohol in silky needles melting at 167°C . Its alcoholic solution gave reddish-violet colour with ferric chloride (Found C, 72.9, H, 6.5, $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 73.1, H, 6.4 per cent)

The *semicarbazone* crystallised from alcohol in small plates melting at 258°C

Trans-octalino-(2' 3' 4 3)-1 2- α -naphthapyrone, obtained from α -naphthol, crystallised from acetic acid in pointed needles melting at 222°C (Found C, 82.6, H, 6.7, $\text{C}_{21}\text{H}_{20}\text{O}_2$ requires C, 82.9, H, 6.6 per cent)

7 *8-Dihydroxy-trans-octalino-(2' 3' 4 3)-coumarin*, obtained from pyrogallol, crystallised from alcohol in prismatic needles melting at 267°C . The coumarin forms a very sparingly soluble sodium salt, and cannot be methylated by dimethyl sulphate. Its alcoholic solution gives deep bluish green coloration with ferric chloride, while concentrated sulphuric acid dissolves it with a yellow colour (Found C, 71.0, H, 6.5, $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3, H, 6.3 per cent).

The *di-acetyl derivative* crystallised from alcohol in fine needles melting at 200°C (Found C, 68.0, H, 5.9, $\text{C}_{21}\text{H}_{22}\text{O}_6$ requires C, 68.1, H, 6.0 per cent).

5 *7-Hydroxy-7-methyl-trans-octalino-(2' 3' 4 3)-coumarin*, prepared from orcinol, was a microcrystalline powder melting at 315°C . It could not be satisfactorily crystallised from any solvent. Its alkaline solution was yellow and non-fluorescent. It could not be methylated by dimethyl sulphate and alkali (Found C, 75.8, H, 7.2, $\text{C}_{18}\text{H}_{20}\text{O}_3$ requires C, 76.1, H, 7.0 per cent).

The *acetyl derivative* crystallised from alcohol in tiny needles melting at 184°C (Found C, 73.4, H, 6.5, $\text{C}_{20}\text{H}_{24}\text{O}_3$ requires C, 73.6, H, 6.7 per cent).

5 *7-Dihydroxy-trans-octalino-(2' 3' 4 3)-coumarin*, obtained from phloroglucinol, crystallised from alcohol in small plates melting at 265°C . Its alcoholic solution gave green coloration with ferric chloride. The yellow, alkaline solution was devoid of fluorescence. It could not be methylated by sulphate and alkali (Found C, 71.1, H, 6.4, $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3, H, 6.3 per cent).

The *diacetyl derivative* crystallised from alcohol in needles melting at 173°C (Found C, 67.9, H, 6.2, $\text{C}_{21}\text{H}_{22}\text{O}_6$ requires C, 68.1, H, 6.0 per cent).

Summary

Coumarins have been prepared from alkylcyclo-hexanone-2-carboxylates and *trans*- β -decalone-3-carboxylate by condensing various dihydric and trihydric phenols either in the presence of concentrated sulphuric acid or phosphorus oxychloride. The Fries' Transformation of the 7-acetoxy-derivatives of the various coumarins has been studied with the purpose of comparing the 7-hydroxy-8-acetyl derivatives with their 7-hydroxy-6-acetyl isomers.

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ON LINEAR TRANSFORMATIONS OF BOUNDED SEQUENCES—II.

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PART II

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§ 7 General Remarks.

THEOREMS II and III of Part I dealt completely with the way in which direct T's combine, and the equivalence of combinations of T's to other transformations defined by matrices. Theorem IV and its complement dealt with the simplest case of combinations of direct T's and inverse T^{-1} 's. In this part we propose to prove some very general theorems on such combinations, in (8) and (9). (10) deals with a subclass of T designated \bar{T} , whose inverses (T^{-1}) behave very much like any direct T, so that Theorems II and III of Part I characterize completely the way in which \bar{T}^{-1} or a product $(\bar{T}_1^{-1} \cdot \bar{T}_2^{-1} \cdot \bar{T}_3^{-1})$ can combine with any T's. In (8) and (9), we will notice that in all the theorems the sequence (x_n) , on which the transformations are applied will be at least a null sequence. In (11) two theorems applicable to bounded sequences, for special subclass of T's are proved. (12) deals with the solution of an integral equation, an adaptation to the continuous variable of Theorem IV of Part I.

As in Part I the matrix defining a T will be denoted by $\|a_{m,n}\|$ where $a_{m,n}$ is characterized by the four conditions of (2.1), and the matrix defining T^{-1} by $\|\beta_{m,n}\|$. The numbering of theorems here is in continuation of the theorems of Part I.

§ 8. General Theorems

THEOREM V. Let S be a transformation defined by $\|c_{m,n}\|$ such that $c_{m,n} = 0$ $n < m$, and R the product of a number of direct T's, i.e., $R = (T_1 T_2 \cdots T_k)$,

defined by $\|d_{m,n}\| = \|a^1_{m,n}\| \cdot \|a^2_{m,n}\| \cdots \|a^k_{m,n}\|$, where $\|a^k_{m,n}\|$ defines T_p and let $\|h_{m,n}\| = \|d_{m,n}\| \cdot \|c_{m,n}\|$. If the set of series $\sum_{n=0}^{\infty} c_{m,n} y_n$ converge uniformly for all m , then

(1) $(R) \cdot [S(y_n)] = (R S)(y_n)$, (2) $\sum_{n=0}^{\infty} h_{m,n} y_n$ converge uniformly for all m , (3) the sequence $S(y_n)$ is a null one

Lemma 1 $\sum_{p=0}^{\infty} |d_{n,n+p}| < k$ for all n ,

Proof — $d_{n,n+p} = \sum \sum a^1_{n,n+p_1} a^2_{n+p_1,n+p_2} \cdots a^k_{n+p_{k-1},n+p}$

Hence $\sum_{p=0}^{\infty} |d_{n,n+p}| < \sum_{p=0}^{\infty} (\sum |a^1_{n,n+p_1}| \cdots |a^k_{n+p_{k-1},n+p}|)$
 $= \sum_{p_1=0}^{\infty} |a^1_{n,n+p_1}| \sum_{p_2=0}^{\infty} |a^2_{n+p_1,n+p_2}| \cdots \sum_{p_{k-1}=0}^{\infty} |a^k_{n+p_{k-1},n+p}|$

Now by condition (d) of 2.1 $\sum_{p=0}^{\infty} |a^r_{n,n+p}| < 2$

Hence $\sum_{p=0}^{\infty} |d_{n,n+p}| < 2^k = k$ [8.1]

Proof of Theorem V — Let $\epsilon > 0$, N_0 so chosen that for all $A > N_0$ and for all $m > 0$

$$\left| \sum_{n=A}^{\infty} c_{m,n} y_n \right| < \epsilon \quad \text{Let } m \text{ be a fixed integer, and } A_0$$

another fixed integer such that $A_0 > N_0$ and $A_0 > m$

$$\text{Let } z_n = \sum_{p=0}^{\infty} c_{m,p} y_p = S(y_n)$$

Then

$$z_m = \sum_{n=0}^{\infty} c_{m,n} y_n = \sum_{n=0}^{A_0} + \sum_{n=A_0+1}^{\infty} = \sum_{n=0}^{A_0} + \theta_m \epsilon.$$

and

$$z_{m+r} = \sum_{n=0}^{A_0} c_{m+r,n} y_n + \theta_{m+r} \epsilon$$

for $m+r < A_0$,

and

$$z_{A_0+k} = \sum_{n=A_0+k}^{\infty} c_{A_0+k,n} y_n = \theta_{A_0+k} \epsilon, \quad [8.2]$$

$$\text{where } -1 < \theta_p < 1.$$

Hence $|z_{A_0+k}| < \epsilon$ for all $k \geq 0$ proving (3) of Theorem V [8.3]

Now $R(z_m) = \sum_{p=0}^{\infty} d_{m,p} z_p = \sum_{p=0}^{A_0} + \sum_{p=A_0+1}^{\infty} = B_1 + B_2. \quad [8.4]$

By (8.1) and (8.3) $|B_2| < k\epsilon$.

$$\begin{aligned}
 \text{By (8.2) } B_1 &= \sum_{p=0}^{p=\Lambda_0} d_{m,p} \left(\sum_{r=0}^{r=\Lambda_0} c_{p,r} y_r + \theta_p \epsilon \right) = \\
 &= \sum_{p=0}^{p=\Lambda_0} d_{m,p} \sum_{r=0}^{r=\Lambda_0} c_{p,r} y_r + \epsilon \sum_{p=0}^{p=\Lambda_0} \theta_p \cdot d_{m,p} \\
 &= \sum_{r=0}^{r=\Lambda_0} (\sum_{p=0}^{p=\Lambda_0} c_{p,r}) y_r + \theta' k \epsilon \quad -1 < \theta' < 1 \\
 &= \sum_{r=0}^{r=\Lambda_0} h_{m,r} y_r + \theta' k \epsilon
 \end{aligned}$$

$$\text{Hence } \sum_{p=0}^{p=\infty} d_{m,p} \cdot z_p = \sum_{r=0}^{r=\Lambda_0} h_{m,r} y_r + \theta'' \cdot 2k \epsilon \quad -1 < \theta'' < 1 \quad [8.5]$$

Making

$\Lambda_0 \rightarrow \infty$ We have

$$\sum_{p=0}^{p=\infty} d_{m,p} z_p = \sum_{r=0}^{r=\infty} h_{m,r} y_r \quad \text{or} \quad [8.6]$$

$$R(z_n) = (R)[S(y_n)] = (RS)(y_n) \quad [8.7]$$

From (8.5) and (8.6) we get $\left| \sum_{r=\Lambda_0+1}^{\infty} h_{m,r} z_r \right| < 2k\epsilon$ proving (2) of theorem V [8.8]

THEOREM VI Let S be any transformation defined by $\|c_{m,n}\|$ such that $c_{m,n} = 0$ for $n < m$, and R_1 the product of a number of direct transformations, i.e., $R_1 = (T_{s_1} T_{s_2} T_{s_p})$ defined by $\|d_{m,n}\| = \|\alpha^s_{m,n}\| \cdots \|\alpha^p_{m,n}\|$, and R_2 the product of number of inverse transformations, i.e., $R_2 = (T_1^{-1} T_2^{-1} T_k^{-1})$ defined by $\|\beta_{m,n}\| = \|\beta^1_{m,n}\| \cdots \|\beta^k_{m,n}\|$ where $\|\beta^s_{m,n}\|$ defines (T_s^{-1}) . Let b_p be the upper bound of $\beta_{m,n+p}$ for all n

and $\sum_0^{p=n} b_p = B_n$. If $\left| \sum_{n=A}^{\infty} c_{m,n} y_n \right| = 0 \left(\frac{1}{B_A} \right)$ for all m and for all sufficiently large A , then

$(R_1 R_2)[S(y_n)] = (R_1 R_2 S)(y_n)$ when the latter exists

Proof —Let m_0 be any positive integer, and Λ_0 sufficiently large and $\Lambda_0 > m_0$

Let $z_n = S(y_n)$

$$\begin{aligned}
 \text{Then } z_{m_0} &= \sum_{n=0}^{n=\infty} c_{m_0,n} y_n = \sum_{n=0}^{n=\Lambda_0-1} + \sum_{n=\Lambda_0}^{\infty} = \sum_{n=0}^{n=\Lambda_0-1} + \frac{\theta_{m_0} \cdot \epsilon_{\Lambda_0}}{B_{\Lambda_0}} \\
 z_{m_0+r} &= \sum_{n=0}^{n=\Lambda_0-1} c_{m_0+r,n} y_n + \theta_{m_0+r} \cdot \frac{\epsilon_{\Lambda_0}}{B_{\Lambda_0}} \quad [8.9]
 \end{aligned}$$

for $m_0 + r < \Lambda_0 - 1$, $-1 < \theta_p < 1$.

Let $\|\gamma_{mn}\| = \|d_{m,n}\| \|\beta_{m,n}\|$

$$\begin{aligned} \text{Then } \sum_{n=m_0}^{n=\Lambda_0-1} \gamma_{m_0, n} z_n &= \sum_{n=m_0}^{n=\Lambda_0-1} \gamma_{m_0, n} \left(\sum_{p=\Lambda_0-1}^{p=\Lambda_0-1} c_n p y_p + \theta_n \epsilon_{\Lambda_0} \right) \\ &= \sum_{p=\Lambda_0-1}^{p=\Lambda_0-1} \left(\sum_{n=m_0} \gamma_{m_0, n} c_n p \right) y_p + \frac{\epsilon_{\Lambda_0}}{B_{\Lambda_0}} \sum_{n=m_0}^{n=\Lambda_0-1} \gamma_{m_0, n} \theta_n = B_1 + B_2 \end{aligned}$$

$$|B_2| \leq \frac{\epsilon_{\Lambda_0}}{B_{\Lambda_0}} \sum_{n=m_0}^{n=\Lambda_0-1} |\gamma_{m_0, n}|, \text{ and } \gamma_{m_0, n} = \sum_{n_1=m_0}^{n_1=n} d_{m_0, n_1} \beta_{n_1, n}$$

$$\begin{aligned} \text{Hence } |\gamma_{m_0, n}| &\leq \sum_{n_1=m}^{n_1=n} |d_{m, n_1}| b_{n-n_1} \text{ and } \sum_{n=m_0}^{n=\Lambda_0-1} |\gamma_{m_0, n}| = \sum_{n=m_0}^{n=\Lambda_0-1} \sum_{n_1=m_0}^{n_1=n} |d_{m_0, n_1}| b_{n-n_1} \\ &= \sum_{k=0}^{\Lambda_0-1-m_0} \frac{1}{b_k} \sum_{n=m_0}^{\Lambda_0-1-\mu} |d_{m_0, n}| \leq k B_{\Lambda_0-1-m_0} \text{ where } \sum_{n=m_0}^{\infty} |d_{m_0, n}| \leq k \text{ by (8.1)} \end{aligned}$$

$$\text{Hence } |B_2| \leq k \frac{B_{\Lambda_0-1-m_0}}{B_{\Lambda_0}} \epsilon_{\Lambda_0} \leq k \epsilon_{\Lambda_0}$$

$$\begin{aligned} \text{Hence } \sum_{n=m_0}^{n=\Lambda_0-1} \gamma_{m_0, n} z_n &= \sum_{p=\Lambda_0-1}^{p=\Lambda_0-1} \left(\sum_{n=m_0} \gamma_{m_0, n} c_n p \right) y_p + \theta k \epsilon_{\Lambda_0} \\ &= \sum_{p=\Lambda_0-1}^{p=\Lambda_0-1} \gamma_{m_0, p}^1 y_p + \theta k \epsilon_{\Lambda_0}, \end{aligned}$$

$$\text{where } \|\gamma_{m, n}^1\| = \|\gamma_{m, n}\| \|\epsilon_{m, n}\|$$

If the series $\sum_{p=0}^{\infty} \gamma_{m_0, p}^1 y_p$ converges, i.e., $(R_1 R_2 S)(y_n)$ exists, then making $\Lambda_0 \rightarrow \infty$ we have

$$\sum_{n=m_0}^{n=\infty} \gamma_{m_0, n} z_n = \sum_{p=0}^{p=\infty} \gamma_{m_0, p}^1 y_p \quad [8.10]$$

i.e., $(R_1 R_2 S)(y_n) = (R_1 R_2 S)(y_n)$ when the latter exists

THEOREM VII Let $R_1 = (T_{q_1} T_{q_2} T_{q_r})$ defined by $\|d_{m, n}\|$, $R_2 = (T_{s_1} T_{s_2} T_{s_p})$ defined by $\|e_{m, n}\|$

$$\|d_{m, n}\| = \|a_{m, n}^{a_1}\| \quad \|a_{m, n}^{a_r}\|, \|e_{m, n}\| = \|a_{m, n}^{s_1}\| \quad \|a_{m, n}^{s_p}\|$$

$$\text{and } I = (T_1^{-1} T_2^{-1} T_k^{-1}) \text{ defined by } \|\beta_{m, n}\| = \|\beta_{m, n}^1\| \quad \|\beta_{m, n}^k\|$$

$$\text{Let } S(R_1 I R_2) \text{ be defined by } \|\gamma_{m, n}\| = \|d_{m, n}\| \|\beta_{m, n}\| \|e_{m, n}\|$$

$$\text{Let the upper bound of } \beta_{m, n+p} \text{ be } b_p, \text{ and } \sum_{p=0}^n b_p = B_n$$

If $y_n = 0 \left(\frac{1}{B_n^{1+\delta}} \right)$ in case B_n diverges, or $y_n = 0$ (1) when B_n con-

verges, then (1) $\sum_{n=0}^{\infty} |\gamma_{m, n} y_n|$ converges uniformly for all m ,

(2) the terms of the product S can be associated in any manner and the resultants of the operations on the sequence y_n are all equal to $S(y_n)$

[for example $(T_{q_1} T_{q_2} T_{q_{r_1}}) (T_{q_{r_1+1}} \dots T_{q_r}) (\dots T_1^{-1} \dots T_l^{-1}) (T_{l+1}^{-1} \dots T_k^{-1})$
 $(T_{s_1} T_{s_p}) (T_{s_{p+1}} \dots T_{s_p}) (y_n) = S(y_n)$]

$$\text{Lemma I} \quad |\gamma_{m,m+p}| \leq \sum_r \sum_k |d_{m,m+r}| |\bar{\beta}_{m+r,m+r+k}| |e_{m+r+k,m+p}| \\
\leq \sum_{k=0}^{k=p} b_k \sum_{r=0}^{r=p-k} |d_{m,m+r}| \cdot |e_{m+r+k,m+p}| \quad [8.11]$$

Lemma II Let the terms of R_1 be associated in any manner

$$\text{i.e., Let } R_1 = (T_{q_1} \dots T_{q_{r_1}}) (T_{q_{r_1+1}} \dots T_{q_{r_2}}) \dots (T_{q_{r_{p-1}+1}} \dots T_{q_r}) \\
= R_1^1 R_2^1 \dots R_p^1$$

and let R_1^1 be defined by $\|d_{m,n}^1\|$, R_2^1 by $\|d_{m,n}^2\|$ and so on

Let f_{mn}^1 = absolute value of d_{mn}^1 i.e. $= |d_{m,n}^1|$ etc

$$\text{If} \quad \|\bar{d}_{mn}\| = \|f_{m,n}^1\| \|f_{m,n}^2\| \dots \|f_{m,n}^p\|$$

$$\text{Then} \quad \sum_{n=0}^{\infty} \bar{d}_{m,n} \leq 2^r \quad [8.12]$$

$$\text{Proof —} \quad \text{Since by 2.1} \quad \sum_{n=0}^{n=\infty} |a_{m,n}| \leq 2 \text{ for all } m$$

$$\sum_{n=0}^{n=\infty} f_{m,n}^1 \leq 2^{r_1}$$

$$\sum_{n=0}^{n=\infty} f_{m,n}^2 \leq 2^{r_2-r_1} \dots$$

$$\text{and} \quad \sum_{n=0}^{n=\infty} f_{m,n}^p \leq 2^{r-r_{p-1}} \quad \text{by 8.1}$$

$$\text{Hence} \quad \sum_{n=0}^{\infty} \bar{d}_{m,n} \leq 2^{r_1} 2^{r_2-r_1} \dots 2^{r-r_{p-1}} = 2^r. \quad [8.13]$$

Proof of (1) Let $A > 0$ be any fixed integer and let B_n diverge, and

let m be any positive integer. Let $|y_n| \leq \frac{K}{B_n^{1+\delta}}$ by hypothesis. Consider

now Case I when $m < A$, i.e., $m+q = A$

$$\sum_{n=A}^{\infty} |\gamma_{m,n}| |y_n| = \sum_{p=q}^{\infty} |\gamma_{m,m+p}| |y_{m+p}| \leq$$

$$K \sum_{p=q}^{p=\infty} b_k \sum_{k=0}^p |d_{m,m+r}| |e_{m+k+r,m+p}| \\
\frac{K}{B_{m+p}^{1+\delta}}$$

$$\begin{aligned}
 &= K \sum_{k=0}^{\infty} b_k \sum_{r=0}^{\infty} |d_{m,m+r}| \sum_{p=q}^{\infty} \frac{|e_{m+k+r,m+p}|}{B_{m+p}^{1+\delta}} = K \sum_{k=0}^{\infty} b_k \phi(k) = \\
 &K \left(\sum_{\Lambda+1}^{\infty} + \sum_{\Lambda+1}^{\infty} \right) \\
 &= K (B_1 + B_2) \quad [8 \cdot 14]
 \end{aligned}$$

Since by 8.1 $\sum_{r=0}^{\infty} |e_{m,r}| \leq 2^p = K_2$, $\sum_{p=q}^{\infty} \frac{|e_{m+k+r,m+p}|}{B_{m+p}^{1+\delta}} < \frac{K_2}{B_{m+q}^{1+\delta}} = \frac{K_2}{B_{\Lambda}^{1+\delta}}$

Hence

$$\begin{aligned}
 B_1 &< K_2 \sum_{k=\Lambda}^{\infty} b_k \sum_{r=0}^{\infty} \frac{|d_{m,m+r}|}{B_{\Lambda}^{1+\delta}} \leq \frac{K_2 K_1}{B_{\Lambda}^{1+\delta}} \sum_{k=\Lambda}^{\infty} b_k \text{ since } \sum |d_{m,m+r}| < K_1 \text{ by} \\
 &\quad (8 \cdot 1) \\
 &= \frac{K_2 K_1}{B_{\Lambda}^{\delta}} \quad [8 \cdot 15]
 \end{aligned}$$

$$B_2 = \sum_{k=1}^{\infty} b_{\Lambda+k} \sum_{r=0}^{\infty} |d_{m,m+r}| \sum_{p=q}^{\infty} \frac{|e_{m+r+\Lambda+k,m+p}|}{B_{m+p}^{1+\delta}}$$

Now $e_{m,n} = 0$ $n < m$ and $m + q = \Lambda$

$$\text{Hence } \sum_{p=q}^{\infty} \frac{|e_{m+r+\Lambda+k,m+p}|}{B_{m+p}^{1+\delta}} = \sum_{p=r+\Lambda+k}^{\infty} \frac{|e_{m+r+\Lambda+k,m+p}|}{B_{m+p}^{1+\delta}} < \frac{K_2}{B_{m+r+\Lambda+k}^{1+\delta}}$$

$$\text{and } \sum_{r=0}^{\infty} \frac{|d_{m,m+r}|}{B_{m+r+\Lambda+k}^{1+\delta}} < \frac{K_1}{B_{m+\Lambda+k}^{1+\delta}}$$

$$\text{Hence } B_2 \leq \sum_{k=1}^{\infty} b_{\Lambda+k} \frac{K_1 K_2}{B_{m+\Lambda+k}^{1+\delta}} < K_1 K_2 \cdot \sum_{k=1}^{\infty} \frac{b_{\Lambda+k}}{B_{\Lambda+k}^{1+\delta}} < \frac{K_1 K_2}{\delta B_{\Lambda}^{\delta}}$$

$$\text{since } \frac{1}{B_{n-1}^{\delta}} - \frac{1}{B_n^{\delta}} \geq \frac{\delta b_n}{B_n^{1+\delta}}.$$

$$\text{Hence } B_1 + B_2 = 0 \left(\frac{1}{B_{\Lambda}^{\delta}} \right) \quad [8 \cdot 16]$$

Case II $m > \Lambda$,

proceeding exactly as above we can prove for all m

$$\sum_{n=0}^{\infty} |\gamma_{mn} y_n| = \sum_{n=m}^{\infty} |\gamma_{mn} y_n| = 0 \left(\frac{1}{B_m^{\delta}} \right)$$

Hence when $m > \Lambda$

$$\sum_{n=\Lambda}^{\infty} |\gamma_{mn} y_n| = \sum_{n=m}^{\infty} |\gamma_{mn} y_n| \text{ since } \gamma_{mn} = 0 \text{ } n < m$$

and $\sum_{n=m}^{\infty} |\gamma_{mn} y_n| = 0 \left(\frac{1}{B_m^{\delta}} \right) = 0 \left(\frac{1}{B_A^{\delta}} \right)$ since $m > A$

Hence in all cases $\sum_{n=A}^{\infty} |\gamma_{m,n} y_n| = 0 \left(\frac{1}{B_A^{\delta}} \right)$. [8 17]

Hence (1) is proved

With regard to (2) of Theorem VII we shall prove a particular case of the associations, the proof being the same in all other cases

To prove $(T_{q_1} T_{q_2} T_{q_{r_1}}) (T_{q_{r_1+1}} T_{q_r}) (T_1^{-1} T_l^{-1}) (T_{l+1}^{-1} T_k^{-1}) \times$
 $\times (T_{s_1} T_{s_p}) (T_{s_{p+1}} T_{s_p}) (y_n) = (T_{q_1} T_{q_r} T_1^{-1} T_k^{-1} T_{s_1} T_{s_p}) (y_n)$
 $= S(y_n)$ [8 18]

Let $(T_{q_1} T_{q_{r_1}})$ be defined by $\|d'_{m,n}\|$, $(T_{q_{r_1+1}} T_{q_r})$ by $\|d''_{m,n}\|$
 $(T_1^{-1} T_l^{-1})$ by $\|\beta'_{m,n}\|$, $(T_{l+1}^{-1} T_k^{-1})$ by $\|\beta''_{m,n}\|$
 $(T_{s_1} T_{s_p})$ by $\|e'_{m,n}\|$, $(T_{s_{p+1}} T_{s_p})$ by $\|e''_{m,n}\|$

and let $\bar{d}_{m,n} = \sum_{n_1} |d'_{m,n_1}| |d''_{n_1,n}|$

and $\bar{e}_{m,n} = \sum |e'_{m,n}| |e''_{m,n}|$

Now $\sum_{n_1} |d'_{m,n_1}| \sum_{n_2} |d''_{n_1,n_2}| \sum_{n_3} \beta'_{n_2,n_3} \sum_{n_4} \beta''_{n_3,n_4} \sum_{n_5} |e'_{n_4,n_5}| \sum_p |e''_{n_5,p}| (y_p)$
 $= \sum_{n_1} (\sum |d'_{m,n_1}| |d''_{n_1,n_2}|) \sum_{n_2} \beta_{n_2,n_4} \sum_{n_5} (\sum |e'_{n_4,n_5}| |e''_{n_5,p}|) |y_p|$
 $= \sum d_{m,n_1} \sum \beta_{n_1,n_2} \sum e_{n_2,p} |y_p| = \sum_p^{\infty} (\sum \bar{d}_{m,n_1} \beta_{n_1,n_2} \bar{e}_{n_2,p}) |y_p|$

Since by (8 13), $\sum_{p=0}^{\infty} \bar{d}_{m,p} < K$ and $\sum \bar{e}_{n,p} < K$

exactly as in the proof of (1) of this theorem, we prove $\sum_p^{\infty} (\sum \bar{d}_{m,n_1} \beta_{n_1,n_2} \bar{e}_{n_2,p}) |y_p|$ converges

Hence

$\sum_{n_1=0}^{\infty} d'_{m,n_1} \sum_{n_2=0}^{\infty} d''_{n_1,n_2} \sum_{n_3=0}^{\infty} \beta'_{n_2,n_3} \sum_{n_4=0}^{\infty} \beta''_{n_3,n_4} \sum_{n_5=0}^{\infty} e'_{n_4,n_5} \sum_{p=0}^{\infty} e''_{n_5,p} y_p$
 $= \sum_p^{\infty} (\sum \sum \sum d'_{m,n_1} d''_{n_1,n_2} \beta'_{n_2,n_3} \beta''_{n_3,n_4} e'_{n_4,n_5} e''_{n_5,p}) y_p = S(y_n)$
 i.e., (8 18) is true [8 19]

We will state here some of the other associations that are equivalent to $S(y_n)$ as they will be needed later

$$\begin{aligned}
 & (T_{q_1} T_{q_2} \cdots T_{q_r} T_1^{-1} \cdots T_l^{-1}) (T_{l+1}^{-1} \cdots T_k^{-1} T_{s_1} \cdots T_{s_p}) (y_n) = \\
 & (T_{q_1} T_{q_2} \cdots T_{q_r}) \cdot (T_1^{-1} \cdots T_k^{-1} T_{s_1} \cdots T_{s_p}) (y_n) = \\
 & (T_{q_1} \cdots T_{q_r} T_1^{-1} \cdots T_k^{-1}) (T_{s_1} \cdots T_{s_p}) (y_n) = \\
 & (T_{q_1} T_{q_l}) (T_1^{-1} T_k^{-1}) (T_{s_1} \cdots T_{s_p}) (y_n) = \\
 & (T_{q_1} T_{q_2} \cdots T_{q_r} T_1^{-1} \cdots T_k^{-1} T_{s_1} \cdots T_{s_p}) (y_n) = S(y_n) \quad [8 \ 20]
 \end{aligned}$$

When B_n converges, then $\sum_{p=0}^{\infty} \beta_{n,n+p} < \infty$ and $B_p = K$ for all n [8 21]

and since $\sum_{p=0}^{\infty} |d_{n,p}| \leq K_1$ and $\sum_{p=0}^{\infty} |e_{n,p}| \leq K_2$

$\sum |y_{n,n+p}| \leq k_1 k_2 = k_4$ Let \bar{y}_A be upper bound of $|y_n|$ for $n \geq A$,
then $\sum_{p=A}^{\infty} |y_{n,p} y_p| \leq k_4 \bar{y}_A$ Hence (1) of Theorem VII in this case is proved

Because of (8.21) (2) of Theorem VII in this case is obvious

THEOREM VIII Let $\|\bar{\beta}_{m,n}\| = \|\beta_{m,n}^1\| \|\beta_{m,n}^2\| \cdots \|\beta_{m,n}^r\|$ define $(T_1^{-1} T_2^{-1} \cdots T_k^{-1})$

Let b_p be the upper bound of $\beta_{n,n+p}$ for all n , and $B_n = \sum_{p=0}^n b_p$ as in Theorem VII

Let $T_{p_1}, T_{p_2}, \dots, T_{p_r}$ be r direct T 's and $\|d_{m,n}\| = \|a_{p_1 m,n}^{p_1}\| \cdots \|a_{p_r m,n}^{p_r}\|$ define $(T_{p_1} T_{p_2} \cdots T_{p_r})$

Let T_0 and T_0^{-1} be defined by $\|a_{m,n}^0\|$ and $\|\beta_{m,n}^0\|$

Let $S = (T_{p_1} T_{p_2} \cdots T_{p_r} T_1^{-1} \cdots T_k^{-1})$ be defined by $\|d_{m,n}\| \cdot \|\bar{\beta}_{m,n}\| = \|c_{m,n}\|$ and let $S' = (S T_0^{-1})$ be defined by $\|c_{m,n}\| \|\beta_{m,n}^0\| = \|y_{m,n}\|$

If $y_n = 0 \left(\frac{1}{B_n} \right) \{i.e., (B_n | y_n) \text{ is a null sequence}\}$, then

$\{S' [T_0 (y_n)]\} = \{S' T_0 (y_n)\} = S(y_n)$, when the latter exists,

Proof Let m and p be two any positive integers and $r_{n,n+\mu}$ be

$$= \sum_{r=\mu+1}^{\infty} |a_{n,n+r}^0| \text{ as in (5.2)}$$

Let \bar{y}_{n_0} be upper bound of $|y_n|$ for all $n \geq n_0$

Let $T_0 (y_n) = z_n$

$$\text{Then } z_m = \sum_{r=0}^{\infty} a_{m,m+r}^0 y_{m+r} = \sum_{r=0}^{\infty} r_{m,m+r}^0 + \sum_{p=1}^{\infty} = \sum_{r=0}^{\infty} r_{m,m+r}^0 + \theta_{m,m+p} \bar{y}_{m+p}$$

$$k \leq p, \quad z_{m+k} = \sum_{r=0}^{\infty} a_{m+k,m+r}^0 y_{m+r} + \theta_{m+k,m+p} \bar{y}_{m+p}$$

$$z_{m+p} = y_{m+p} + \theta_p r_{m+p,n+p} \bar{y}_{n+p} \quad [8.22]$$

Consider now

$$\begin{aligned} \sum_{r=0}^p \gamma_{m,m+r} z_{m+r} &= \sum_{r=0}^{r=p} \gamma_{m,m+r} \sum_{s=0}^{s=p} a_{m+r,m+s}^0 y_{m+s} + \bar{y}_{m+p} \sum \theta_r \gamma_{m,m+r} r_{m+r,m+p} \\ &= A + B \\ A &= \sum_{r=0}^{s=p} (\sum_r \gamma_{m,m+r} a_{m+r,m+s}^0) y_{m+s} = \sum_{s=0}^{s=p} c_{m,m+s} y_{m+s} \end{aligned} \quad [8.23]$$

$$|B| \leq \bar{y}_{m+p} \sum_{r=0}^p |\gamma_{m,m+r}| \cdot r_{m+r,m+p} = y_{m+p} \cdot B_2 \quad [8.24]$$

Now

$$\begin{aligned} \gamma_{m,m+r} &= c_{m,m+k} \beta_{m+k,m+r}^0 \\ B_2 &\leq \sum_{r=0}^p \left(\sum_{k=0}^{k=r} |c_{m,m+k}| \cdot \beta_{m+k,m+r}^0 \right) r_{m+r,m+p} \\ &= \sum_{k=0}^p |c_{m,m+k}| \sum_{r=k}^{r=p} \beta_{m+k,m+r}^0 r_{m+r,m+p} \end{aligned}$$

Just as in the course of proof of Theorem IV in (5.4) and (5.5), by (4.6) of Part I

$$\text{we have } \sum_{r=0}^p \beta_{m,m+r}^0 r_{m+r,m+p} \leq 1 \text{ for all } m \text{ and all } p$$

$$B_2 \leq \sum_{k=0}^p |c_{m,m+k}| \text{ and } c_{m,m+k} = \sum_{s=0}^k d_{m,m+s} \bar{\beta}_{m+s,m+k}$$

$$\text{Hence } \sum_{k=0}^{k=p} |c_{m,m+k}| \leq \sum_{k=0}^{k=p} \sum_{s=0}^{s=k} |d_{m,m+s}| \bar{\beta}_{m+s,m+k}$$

$$\begin{aligned} \text{Now } \bar{\beta}_{m,m+r} &\leq b_r \text{ Hence } \sum_{k=0}^{k=p} |c_{m,m+k}| \leq \sum_{k=0}^{k=p} \sum_{s=0}^{s=k} |d_{m,m+s}| b_{k-s} \\ &= \sum_{n=0}^{n=p} b_n \sum_{r=0}^{r=n} |d_{m,m+r}| \end{aligned}$$

Now by Lemma of (8.1) we have $\sum_{r=0}^{\infty} |d_{m,m+r}| \leq K$, a constant

$$\text{Hence } B_2 \leq K \cdot B_p \quad [8.25]$$

$$\text{Now } |B| \leq y_{m+p} |B_2| \leq K B_p \cdot y_{m+p} = \frac{K \cdot B_p \cdot \epsilon_{m+p}}{B_{m+p}} \leq K \epsilon_{m+p}$$

since $y_n = 0 \left(\frac{1}{B_n} \right)$

$$\text{Hence } \sum_{r=0}^{r=p} \gamma_{m,m+r} z_{m+r} = \sum_{s=0}^{s=p} c_{m,m+s} y_{m+s} + \theta K \epsilon_{m+p} \quad [8.26]$$

If the second series $\sum_{s=0}^{s=\infty} c_{m,m+s} y_{m+s}$ converges, then

$$\sum_{r=0}^{r=\infty} \gamma_{m,m+r} z_{m+r} = \sum_{s=0}^{s=\infty} c_{m,m+s} y_{m+s} \quad [8.27]$$

$$\text{i.e., } S' [T_0(y_n)] = (S' T_0)(y_n) = S(y_n) \text{ when the latter exists} \quad [8.28]$$

THEOREM IX Let S , S' and T_0 be as in (8.21) and R be $= (T_{q_1} T_{q_2} T_{q_r})$ defined by

$$\|e_{m,n}\| \quad \text{Then also } (S') [(T_0 R) (y_n)] = (S' T_0 R) (y_n) \\ = (SR) (y_n) \text{ if the latter exists}$$

$$y_n = 0 \left(\frac{1}{B_n} \right)$$

Proof Let $R (y_n) = z_n$ and $\bar{y}_{n_0} =$ upper bound of $|y_n|$ for $n > n_0$

$$\text{then } |z_n| = \left| \sum_{\rho=n}^{\infty} e_{n\rho} y_\rho \right| \leq \bar{y}_n \cdot \sum_{\rho=n}^{\infty} |e_{n\rho}| < K \bar{y}_n = 0 \left(\frac{1}{B_n} \right)$$

$$\text{Hence } z_n = 0 \left(\frac{1}{B_n} \right). \quad [8.29]$$

Now $(T_0 R) (y_n) = T_0 (z_n)$ and

$$S' [T_0 (z_n)] = (S' T_0) (z_n) = S (z_n) \\ = S [R (y_n)] \text{ (if the latter exists)} \quad [8.30]$$

$$\text{Now the series } \sum_{\rho=n}^{\infty} |e_{n\rho}| y_n \leq \bar{y}_n \cdot K = 0 \left(\frac{1}{B_n} \right)$$

$$\text{since } \sum_{\rho=n}^{\infty} |e_{n\rho}| \leq K \text{ by 8.1}$$

Hence by Theorem VI $S R (y_n) = (SR) (y_n)$ when the latter exists [8.31]

A particularly interesting case of Theorem IX is when $T_1^{-1} = T_2^{-1} \dots = T_k^{-1} =$ unit transformation, then the theorem would be

THEOREM X If $S = (T_{s_1} T_{s_2} T_{s_p})$ and y_n a null sequence and $R = (T_{q_1} T_{q_2} T_{q_r})$ then $(S T_0^{-1}) [(T_0 R) (y_n)] = (SR) (y_n)$ [8.32]

§ 9. On Combinations of Inverse (T^{-1}) Transformations

Most of the theorems in this section are either deductions from, or particular cases of theorems of previous section

THEOREM XI Let $R_1 = (T_{q_1} T_{q_2} T_{q_r})$ defined by $\|d_{mn}\| = \|a_{q_1, m, n}\| \cdot \|a_{q_r, m, n}\|$

$$R_2 = (T_{s_1} \cdot T_{s_2} \dots T_{s_p}) \cdot \dots \quad \|e_{m,n}\| = \|a_{s_1, m, n}\| \cdot \|a_{s_p, m, n}\|$$

$$I = (T_1^{-1} T_2^{-1} T_k^{-1}) \dots \quad \|\bar{\beta}_{m,n}\| = \|\beta_{m,n}^1\| \cdot \|\beta_{m,n}^k\|$$

$$\text{and} \quad S = (I R_2) \text{ defined by } \|c_{m,n}\| = \|\bar{\beta}_{m,n}\| \cdot \|e_{m,n}\|$$

If $\sum_{n=\infty}^{\infty} c_{m,n} y_n$ converges uniformly for all m , then

$$(R_1) \cdot [S (y_n)] = (R_1 S) (y_n) \quad [9.1]$$

This is a particular case of Theorem V and result follows from (8.7).

THEOREM XII Let $S = (T_1^{-1} T_k^{-1})$ defined by $\|\tilde{\beta}_{m,n}\|$

If $\sum_{n=\infty}^{\infty} \tilde{\beta}_{m,n} y_n$ converges uniformly for all m , then

$$(1) (T_l T_{l-1} \cdots T_1) (T_1^{-1} \cdots T_k^{-1}) (y_n) = (T_{l+1}^{-1} \cdots T_k^{-1}) (y_n) \quad 0 \leq l \leq k$$

$$(2) (T_k T_{k-1} \cdots T_1) (T_1^{-1} \cdots T_k^{-1}) (y_n) = y_n$$

$$(3) (T_1^{-1} T_2^{-1} \cdots T_k^{-1}) (y_n) = (T_1^{-1}) (T_2^{-1}) (T_l^{-1}) (T_{l+1}^{-1} \cdots T_k^{-1}) (y_n) \\ = (T_1^{-1}) (T_2^{-1}) \cdots (T_k^{-1}) (y_n)$$

Proof

$$(1) \text{ is a particular case of (8.33)} \quad [9.2]$$

$$(2) \text{ is a particular case of (1) when } l = k. \quad [9.3]$$

$$(3) \text{ Let } z_m = \sum_{n=\infty}^{\infty} \tilde{\beta}_{mn} y_n \text{ then by (1) } (T_l T_{l-1} \cdots T_1) (z_m) = \\ (T_{l+1}^{-1} \cdots T_k^{-1}) (y_n) = \varepsilon_m$$

Since $\sum \tilde{\beta}_{m,n} y_n$ is uniformly convergent by (3) of theorem V it is a null sequence. By repeated application of Theorem IV of Part I as in corollary to it

$$z_m = \sum_{r_1=\infty}^{\infty} \beta_{m,m+r_1}^{r_1} \sum_{r_2=\infty}^{\infty} \beta_{m+r_1,m+r_2}^{r_2} \cdots \sum_{p=\infty}^{\infty} \beta_{m+r_1+\cdots+r_{p-1},m+p}^{r_p} = \\ = (T_1)^{-1} \cdots (T_l)^{-1} (\varepsilon_m) = (T_1)^{-1} (T_2)^{-1} \cdots (T_l)^{-1} (T_{l+1}^{-1} \cdots T_k^{-1}) (y_n) \quad [9.4]$$

and in particular when $l = k$ $z_m = (T_1)^{-1} (T_2)^{-1} \cdots (T_k^{-1}) (y_n)$

$$= \sum_{r_1=\infty}^{\infty} \beta_{m,m+r_1}^{r_1} \sum_{r_2=\infty}^{\infty} \beta_{m+r_1,m+r_2}^{r_2} \cdots \sum_{p=\infty}^{\infty} \beta_{m+r_1+\cdots+r_{p-1},m+p}^{r_p} y_p \\ = \sum_{p=\infty}^{\infty} \beta_{m,m+p}^{p} y_p \quad [9.5]$$

A particularly interesting case of Theorem VI is the following

THEOREM XIII Let $R_1 = (T_{s_1} T_{s_2} T_{s_3} \cdots T_{s_p})$, be defined by $\|d_{mn}\|$

$$\text{and } R_2 = (T_1^{-1} \cdots T_k^{-1}) \quad \|\beta_{m,n}\|$$

and $S = (T_{p_1}^{-1} \cdots T_{p_l}^{-1} T_{q_1} T_{q_2} \cdots T_{q_r})$ defined by $\|c_{m,n}\|$

$$\text{If } \left| \sum_{n=\infty}^{\infty} c_{m,n} y_n \right| = 0 \left(\frac{1}{B_A} \right) \text{ for all } m$$

then $(R_1 R_2) [S(y_n)] (R_1 R_2 S)(y_n)$ when the latter exists [9.6]

THEOREM XIV Let $(T_1^{-1} T_2^{-1} T_k^{-1})$ be defined by $\|\tilde{\beta}_{m,n}\|$ then if $\sum \tilde{\beta}_{mk} \|y_n\|$ converges for all m , then the terms of the product $(T_1^{-1} \cdots T_k^{-1})$ can be associated in any arbitrary manner, and the resultant of all the associations on y_n is equal to $(T_1^{-1} T_2^{-1} T_k^{-1}) (y_n)$

We shall take a particular association and prove it, the proof for all other associations being the same.

$$\begin{array}{ll} \text{Let } (T_1^{-1} \ T_2^{-1} \ T_{l_1}^{-1}) \text{ be defined by } \|\beta'_{m,n}\| & \\ (T_{l_1+1}^{-1} \ \dots \ T_{l_2}^{-1}) & \|\beta''_{m,n}\| \\ (T_{l_2+1}^{-1} \ \dots \ T_k^{-1}) & \|\beta'''_{m,n}\| \end{array}$$

$$\text{To prove } \sum_{n_1=0}^{\infty} \beta'_{m,n_1} \sum_{n_2=0}^{\infty} \beta''_{n_1,n_2} \sum_{p=0}^{\infty} \beta'''_{n_2,p} y_p = \sum_{p=0}^{\infty} \beta_{m,p} y_p$$

Now all the $\beta_{m,n} > 0$, and $\|\beta'_{m,n}\| \|\beta''_{m,n}\| \|\beta'''_{m,n}\| = \|\beta_{m,n}\|$

Since $\sum \beta_{m,p} |y_p|$ converges

$$\begin{aligned} \sum_{p=0}^{\infty} \beta_{m,p} y_p &= \sum_{p=0}^{\infty} (\sum \beta'_{m,p_1} \beta''_{p_1,p_2} \beta'''_{p_2,p}) y_p \\ &= \sum_{p_1=0}^{\infty} \beta'_{m,p_1} \sum_{p_2=0}^{\infty} \beta''_{p_1,p_2} \sum_{p=0}^{\infty} \beta'''_{p_2,p} y_p \\ & \text{ i.e., } (T_1^{-1} \ T_2^{-1} \ T_{l_1}^{-1}) (T_{l_1+1}^{-1} \ \dots \ T_{l_2}^{-1}) (T_{l_2+1}^{-1} \ \dots \ T_k^{-1}) (y_n) \\ &= (T_1^{-1} \ \dots \ T_k^{-1}) (y_n) \end{aligned} \quad [9 \ 7]$$

THEOREM XV $\|\beta_{m,n}\|$ defines $(T_1^{-1} \ \dots \ T_k^{-1})$. If $\sum \beta_{m,n} |y_n|$ converges uniformly for all m then (1), (2), (3) of Theorem XII and the conclusion of XIV are all true in this case

This is obvious. An interesting case of this is when $y_n = 0 \left(\frac{1}{B_n^{1+\delta}} \right)$ for by Theorem VII $\sum \beta_{m,n} |y_n|$ converges uniformly if $y_n = 0 \left(\frac{1}{B_n^{1+\delta}} \right)$ [9 8]

§ 10 On the Properties of a Particular Subclass of (T)

We notice that in the theorems proved till now, in order that a combination of inverse and direct transformations on a sequence $\{y_n\}$ may be valid, there must be some strict restriction on y_n (for e.g., in Theorem IV, $y_n \rightarrow 0$ as $n \rightarrow \infty$). In general, when a combination involves an inverse, the restriction on y_n is greater than when the combination is purely of direct T's in which latter case the only restriction being y_n be bounded. In § 10 we deal with a subclass of (T) designated by \bar{T}_0 . The algebra of combinations involving any number of T's and $(\bar{T})^{-1}$ is very simple and exactly like that of direct (T) transformation combinations

The matrix $\|\bar{a}_{m,n}\|$ of a \bar{T} is characterised by the following

$$(a) \ \bar{a}_{nn} = 1 \ (b) \ \bar{a}_{m,n} = 0, \ n < m \ (c) \ \bar{a}_{m,n} \leq 0, \ n > m \text{ and}$$

$$(d) \quad - \sum_{p=1}^{\infty} \bar{a}_{m,m+p} \leq k < 1 \text{ for all } m, \text{ where the first three condi-}$$

tions are the same as in (2.1) for a T and (d) is a greater restriction than (d) of (2.1) [10.1]

From (4.7) if $\|\beta_{mn}\|$ defines a $(\bar{T})^{-1}$ then $\sum_{p=0}^{\infty} \beta_{m, m+p} \leq \frac{1}{1-k}$. [10.2]

Let us designate the matrix of any T , \bar{T} or $(\bar{T})^{-1}$ by $\|b_{mn}\|$. Then from (10.1), and (10.2) and condition (d) of (2.1) we have $\sum_{p=0}^{\infty} |b_{m, m+p}| < K$ (a constant) for all m . [10.3]

If V stands for any T , \bar{T} , or $(\bar{T})^{-1}$ the most general theorem involving T , \bar{T} and $(\bar{T})^{-1}$ will be the following

THEOREM XVI If $\{x_n\}$ be $\left\{\frac{\text{bounded}}{\text{null}}\right\}$ sequence so is $(V_1, V_2 \dots V_k)(x_n)$, and $(V_1 V_2 \dots V_k)(x_n) = (V_1 V_2 \dots V_p) \cdot (V_{p+1} \dots V_l) \cdot (V_{l+1} \dots V_k)(x_n)$. Proof is immediate because it means that all $(\bar{T})^{-1}$ behave exactly like the direct transformation T . [10.4]

In particular it is interesting to notice the form which Theorem IV and its complement take in the case of \bar{T} and T^{-1}

THEOREM XVII $\{x_n\}$ being a bounded sequence, if $\bar{T}(x_n) = y_n$, then

$$(1) x_n = (\bar{T})^{-1}(y_n),$$

(2) Given $\{y_n\}$ the infinite set of equations $T(x_n) = \sum \bar{a}_{m,p} x_p = y_m$, $m = 0, 1, 2, \dots, n$,—under the restriction x_n be bounded, has utmost one solution.

(3) The necessary and sufficient condition that the infinite set of equations $\sum \bar{a}_{m,p} x_p = y_m$ has one solution $\{x_n\}$ under the restriction that x_n be bounded is that y_n be bounded

The proofs of (1), (2) and (3) follow very simply from Theorem XI [10.5]

§ 11 Two theorems applicable for a special subclass of (T) .

Let T_0 be defined by $\|a_{m,n}^0\|$ and T_0^{-1} by $\|\beta_{m,n}^0\|$

Let S be any transformation denoted by $\|s_{m,n}\|$ where $s_{m,n} = 0$, $n < m$,

THEOREM XVIII · If (1) $\{x_n\}$ be a bounded sequence and (2) $\frac{s_{m, m+p}}{\beta_{m, m+p}^0} \rightarrow 0$ as $p \rightarrow \infty$ for every m and (3) $|s_{m,n}| \leq K'$ for all m, n , then $S[T_0(x_n)] = (S T_0)(x_n)$, when the latter exists.

Proof:

Let $|x_n| < K$. Let $\sum_{p=p+1}^{\infty} |a_{m, n+p}^0| = \sum_{p=p+1}^{\infty} a_{m, n+p}^0 = r_{m, n+p}$, $p \geq 1$

and let $T_0(x_n) = y_n$.

$$\text{Then } y_n = \sum_{\rho=0}^{\infty} a_{n,n+\rho}^0 x_{n+\rho} = \sum_{\rho=0}^p + \sum_{\rho+1}^{\infty} = {}^p\bar{\Sigma}^p + \theta K \cdot r_{n,n+p}$$

$$\text{Similarly } y_{n+k} = \sum_{\rho=0}^p a_{n+k,n+\rho}^0 x_{n+\rho} + \theta_k K r_{n+k,n+p} \quad [11.1]$$

for $k = 0, 1, 2, p$ and $-1 \leq \theta_k \leq 1$.

$$\begin{aligned} \text{Then } \sum_{\rho=0}^p s_{n,n+\rho} y_{n+\rho} &= \sum_{\rho=0}^p s_{n,n+\rho} \cdot \sum_{\rho'=0}^p a_{n+\rho,n+\rho'}^0 x_{n+\rho'} + \\ &= A + B \end{aligned} \quad [11.2]$$

$$A = \sum_{\rho'=0}^p \left(\sum_{\rho=0}^p s_{n,n+\rho} a_{n+\rho,n+\rho'}^0 \right) x_{n+\rho'}$$

$$|B| \leq K \cdot \sum_{\rho=0}^p |s_{n,n+\rho}| r_{n+\rho,n+p} = K \left(\sum_{k=0}^{p-1} + \sum_k^p \right) = K (\beta_1 + \beta_2),$$

choose k sufficiently large such that for $\rho \geq k$, $\frac{|s_{n,n+\rho}|}{\beta_{n,n+\rho}^0} \leq \epsilon$

$$B_2 \leq \epsilon \cdot \sum_{\rho=k}^p \beta_{n,n+\rho}^0 \cdot r_{n+\rho,n+p} \leq \epsilon \sum_{\rho=0}^p \beta_{n,n+\rho}^0 r_{n+\rho,n+p}$$

$$\text{Now } r_{n,n+p} = \sum_{\rho+1}^{\infty} - a_{n,n+\rho}^0 = \sum_{\rho=1}^{\infty} - \sum_{\rho=0}^p \leq R_{n,n+p} \text{ of (4.6a)}$$

$$\text{and by (4.6a) } \sum \beta_{n,n+\rho}^0 R_{n+\rho,n+p} = 1, \text{ Hence } B_2 \leq \epsilon \quad [11.3]$$

$$\text{Now } B_1 \leq K' \sum_{\rho=0}^{p-k-1} r_{n+\rho,n+p} \text{ by hypothesis (3).}$$

Now each of the sequences $r_{n,n+p}, r_{n+1,n+p}, \dots, r_{n+k-1,n+p}$ tends to zero by condition (d) of 2.1, choosing p sufficiently large, $B_1 \leq \epsilon$

$$\text{Hence for sufficiently large } p \quad |B| \leq \epsilon (\rho) \text{ and we have} \quad [11.4]$$

$$\begin{aligned} \sum_{\rho=0}^p s_{n,n+\rho} y_{n+\rho} &= \sum_{\rho=0}^p \left(\sum_{\rho_1=0}^p s_{n,n+\rho_1} a_{n+\rho_1,n+\rho}^0 \right) x_{n+\rho} + \theta \epsilon (p) \\ &= \sum_{\rho=0}^p d_{n,n+\rho} x_{n+\rho} + \theta \epsilon (p) \end{aligned} \quad [11.5]$$

$$\text{where } \|d_{m,n}\| = \|s_{m,n}\| \cdot \|a_{m,n}^0\|$$

If the latter series $\sum_{\rho=0}^{\infty} d_{n,\rho} x_{\rho}$ converges then in the limit making $p \rightarrow \infty$

$$\sum_{\rho=0}^{\infty} s_{n,n+\rho} y_{n+\rho} = \sum_{\rho=0}^{\infty} d_{n,n+\rho} x_{n+\rho} \text{ or}$$

$$S [T_0(x_n)] = (S T_0)(x_n) \text{ when the latter exists} \quad [11.6]$$

THEOREM XIX Let T_1 and T_2 and $(T_1 T_2)$ be defined by $\|a_{m,n}\|$, $\|b_{m,n}\|$ and $\|c_{mn}\| = \|a_{m,n}\| \|b_{m,n}\|$

$$\text{Let } (1) \sum_{p=p+1}^{\infty} |a_{m,m+p}| = r_{m,m+p}^a$$

$$(2) \sum_{p=p+1}^{\infty} |c_{m,m+p}| = r_{m,m+p}^c$$

and T_1^{-1} be defined by $\|\beta_{m,n}\|$

Then if (1) $\frac{r_{m,m+p}^c}{r_{m,m+p}^a} \rightarrow 0$ as $p \rightarrow 0$ uniformly for all m (2) $\beta_{n,n+p} \rightarrow 0$ as $p \rightarrow \infty$

and (3) $|x_n| \leq K$, then

$$(T_1^{-1} \cdot) [(T_1 T_2) (x_n)] = T_2 (x_n) \quad [11 \ 7]$$

Proof Let $(T_1 T_2) (x_n) = y_n$ and p a positive integer

$$\text{and } y_n = \sum_{p=0}^{\infty} c_{n,n+p} x_{n+p} = \sum_{p=0}^{\infty} \beta_{n,n+p} x_{n+p} = \sum_{p=0}^{\infty} \beta_{n,n+p} r_{n,n+p}^c x_{n+p}$$

$$\text{Similarly } y_{n+k} = \sum_{p=0}^{\infty} c_{n+k,n+p} x_{n+p} + K \theta_k r_{n+k,n+p}^c \quad [11 \ 8]$$

for $k = 0, 1, p$ and $-1 \leq \theta_k \leq 1$

$$\sum_{p=0}^{\infty} \beta_{n,n+p} y_{n+p} = \sum_{p=0}^{\infty} \beta_{n,n+p} \cdot \sum_{s=0}^{\infty} c_{n+p,n+s} x_{n+s} + K \sum_{p=0}^{\infty} \beta_{n,n+p} r_{n+p,n+p}^c x_{n+p}$$

$= A + B$

$$A = \sum_{s=0}^{\infty} \left(\sum_{p=0}^{\infty} \beta_{n,n+p} c_{n+p,n+s} \right) \cdot x_{n+s} = \sum_{s=0}^{\infty} b_{n,n+s} x_{n+s}$$

$$|B| \leq K \left(\sum_{p=0}^{\infty} \beta_{n,n+p} r_{n+p,n+p}^c + \sum_{p=k+1}^{\infty} \right) = K (B_1 + B_2) \quad [11 \ 9]$$

Choosing k large enough such that $\frac{r_{n,n+p}^c}{r_{n,n+p}^a} \leq \epsilon$ for all n and $p > k$

$$B_1 \leq \epsilon \sum_{p=0}^{\infty} \beta_{n,n+p} r_{n,n+p}^a$$

$$\leq \epsilon \sum_{p=0}^{\infty} \beta_{n,n+p} r_{n,n+p}^a \leq \epsilon \quad \text{just as in (12.3).} \quad [11 \ 10]$$

$$\text{and } B_2 = \sum_{p=p-k+1}^{\infty} \beta_{n,n+p} r_{n,n+p}^c \leq K_1 \sum_{p=p-k+1}^{\infty} \beta_{n,n+p}$$

since by condition (d) of (2.1) for T_1 and T_2 , $r_{n,p}^c \leq K_1$ for all n and p .

Choosing p sufficiently large, by condition (2) of Theorem XIX, we have

$$\sum_{\rho=p-k+1}^{\rho=p} \beta_{n,n+p} \leq \epsilon, \text{ i.e., } B_2 \leq \epsilon' (p)$$

Hence [11 11]

$$|B| \leq \epsilon'' (p)$$

and $\sum_{\rho=p}^{\rho=p} \beta_{n,n+p} y_{n+p} = \sum_{\rho=p}^{\rho=p} b_{n,n+p} x_{n+p} + \theta \epsilon'' (p)$

and in the limit $\sum_{\rho=\infty}^{\rho=\infty} \beta_{n,n+p} y_{n+p} = \sum_{\rho=\infty}^{\rho=\infty} b_{n,n+p} x_{n+p}$ or [11 12]

$$(T_1^{-1}) [(T_1 T_2) (x_n)] = T_2 (x_n)$$

§ 12 On an Integral Equation

Corresponding to a T for a sequence, we define the following transformation for the continuous variable

Let (1) $K(x, t) \geq 0$ for all $x \geq 0, t \geq 0$, (2) $K(x, t) = 0, t < x$,

(3) $K(x, t)$ being continuous in (x, t) , for all $x \geq 0, t \geq 0$

(4) $\int_0^\infty K(x, t) dt \leq 1$ for all x [12 1]

Let $u(t)$ be a given continuous function defined for $t \geq 0$, then the trans-

formation T will be $T(u) = u(t) - \int_0^\infty K(t, r) u(r) dr = v(t)$ [12 2]

We discuss here only the existence of the inverse of this transform and show that under certain conditions $u(t) = T^{-1}\{v(t)\}$. The main point of interest in the solution of the integral equation in u of (12.2) is that the range is infinite. We shall show that the solution can be given in terms of Volterra's reciprocal of $K(x, t)$ just as in the ordinary case of finite range when $v(t)$ satisfies a certain condition

THEOREM XX (1) If $u(x) \rightarrow 0$ as $x \rightarrow \infty$ and

$$T(u) = u(x) - \int_0^\infty K(x, t) u(t) dt = v(x),$$

then $u = T^{-1}\{v(x)\} = v(x) + \int_0^\infty \bar{K}(x, t) v(t) dt$

where $[\bar{K}(x, t)] = K(x, t) + K_1(x, t) + \dots + K_n(x, t) + \dots$

where $[\bar{K}_n(x, t)] = \int_0^t K_{n-1}(x, u) K(u, t) du.$

(2) Given $v(x)$, the equation $T(u) = v$ will have utmost one solution under the restriction $u(x) \rightarrow 0$ as $x \rightarrow \infty$

(3) Given $v(x)$ the necessary and sufficient condition that the equation $T(u) = v$ has one solution under the restriction $u(x) \rightarrow 0$ as $x \rightarrow \infty$ is that

$$\int_0^{\infty} \bar{K}(x, t) v(t) dt \text{ converges uniformly for all } x > 0$$

Lemmas.

(1) $K_n(x, t) = 0 \quad t < x$ (proof by mathematical induction and (2) of (12.1) [12.3])

(2) $K_n(x, t) > 0$ for x and t , obvious from definition [12.4]

(3) By definition $K_n(x, t) = \int_0^t K_{n-1}(x, u) K(u, t) du$ To prove

$$K_n(x, t) = \int_0^t K_{n-1}(u, t) K(x, u) du, \quad [12.5]$$

suppose this is true for $1, 2, \dots, n-1$, then we will prove it is true for n and hence for all $n > 1$ since it is true for $n \geq 1$.

By definition $K_n(x, t) = \int_0^t K(u, t) K_{n-1}(x, u) du$

and by hypothesis $K_{n-1}(xu) = \int_0^t K_{n-2}(u, t) K(xu) du$.

$$\begin{aligned} \text{Hence } K_n(x, t) &= \int_0^t K(u, t) du \int_0^u K(xv) K_{n-2}(v, u) dv \\ &= \int_0^t K(x, v) dv \int_v^t K(u, t) K_{n-2}(vu) du \\ &= \int_0^t K(x, v) dv \int_0^t K(u, t) K_{n-2}(v, u) du \\ &\quad \text{since } K_n(v, u) = 0 \quad u < v \\ &= \int_0^t K(x, v) K_{n-1}(vt) dt \end{aligned} \quad [12.5]$$

for $n = 1$. (12.5) is obvious since $K_n(x, t) = K(x, t)$. Hence (12.5) is true for $n \geq 1$.

(4) $\sum_0^{\infty} K_n(x, t)$ converges. This follows from continuity of $K(x, t)$ in $x > 0, t > 0$ [12.6]

(5) $\bar{K}(x, t)$ is continuous; this follows from uniform convergence of $\sum K_n$ and continuity of K_n [12.7]

(6) (1) $\bar{K}(x, t) > 0$ for all x, t , (2) $\bar{K}(x, t) = 0$ $t < x$ (1) is obvious, (2) follows from (12.3).

(7) The reciprocal function $\bar{K}(x, t)$ satisfies two integral equations.

$$K(x, t) - K(x, t) = \int_0^t K(x, u) K(u, t) dt = \int_0^t \bar{K}(u, t) K(x, u) du$$

This follows immediately from definition of K_n and (12.5), and term by term integration of $\Sigma K_n(x)$ [12.8]

(8) Let $R(x, A) = 1 - \int_0^A K(x, t) dt$ To prove

$$\int_0^A K(x, u) R(u, A) du = 1 - R(x, A) \quad [12.9]$$

$$\begin{aligned} \text{Proof } \int_0^A K(x, u) \left\{ 1 - \int_0^A K(u, t) dt \right\} du &= \int_0^A \bar{K}(x, u) du \\ &\quad - \int_0^A K(x, u) \left\{ \int_0^A K(u, t) dt \right\} du = \alpha - \beta \end{aligned}$$

$$\begin{aligned} \beta &= \int_0^A \bar{K}(x, u) du \int_u^A K(u, t) dt, \text{ since } K(u, t) = 0 \quad t < u \\ &= \int_0^A dt \int_0^t \bar{K}(x, u) K(u, t) du = \int_0^A \{K(x, t) - K(x, t)\} dt \text{ by (12.8)} \end{aligned}$$

$$\text{Hence } \alpha - \beta = \int_0^A K(x, t) dt = 1 - R(x, A)$$

$$= \int_0^A \bar{K}(x, u) R(u, A) du \quad [12.9]$$

(12.9) corresponds to formula (4.7) in Part I

Proof (1) of Theorem XX —

$$\begin{aligned} \int_0^A \bar{K}(xt) v(t) dt - \int_0^A \bar{K}(x, t) u(t) dt - \int_0^A \bar{K}(x, t) dt \int_0^\infty \bar{K}(t, z) u(z) dz &\text{ by (12.2)} \\ &= B_1 - B_2 \end{aligned} \quad [12.10]$$

Let $\bar{u}(z_0)$ be the upper bound of $|u(z)|$ for $z > z_0$

$$\text{then } \int_0^\infty K(tz) u(z) dz = \int_0^A + \int_A^\infty = \int_0^A + \theta \cdot r(t, A) \cdot \bar{u}(A_0), \quad [12.11]$$

where $r(t, A) = \int_0^\infty K(tz) dz$ and $-1 \leq \theta \leq 1$.

$$\begin{aligned} \text{Hence } B_2 &= \int_0^A \bar{K}(x, t) dt \int_0^A K(tz) dz + \bar{u}(A) \cdot \int_0^A \theta \bar{K}(x, t) \cdot r(t, A) dt \\ &= C_1 + C_2 \end{aligned} \quad [12.12]$$

$$\text{Now } r(t, A) = \int_0^\infty K(t, z) dz - \int_0^A K(tz) dz \leq 1 - \int_0^A = R(t, A)$$

$$\text{Hence } |c_2| \leq \bar{u}(A) \cdot \int_0^A K(x, t) R(t, A) dt = \bar{u}(A) \{1 - R(x, A)\} \text{ by (12.9)}$$

$$\begin{aligned} \text{and } c_1 &= \int_0^A \bar{K}(x, t) dt \int_t^z K(tz) \cdot u(z) dz \text{ since } K(tz) = 0, \quad z < t \\ &= \int_0^A u(z) dz \cdot \int_0^z \bar{K}(x, t) K(t, z) dt \\ &= \int_0^A (\bar{K}(x, z) - K(x, z)) \cdot u(z) dz \end{aligned} \quad [12.13]$$

$$\text{Hence } B_1 - B_2 = \int_0^A K(x, z) u(z) dz + \theta' u(A) \{1 - R(x, A)\} \quad [12.14]$$

$$\begin{aligned} &= \int_0^\infty K(x, z) \bar{u}(z) dz + \theta'' R(x, A) u(A) + \theta' \{1 - R(x, A)\} \bar{u}(A) \\ &= \int_0^\infty \bar{K}(x, z) u(z) dz + \theta''' \bar{u}(A) \end{aligned} \quad [12.15]$$

$$\begin{aligned} \text{Hence } \int_0^A \bar{K}(xt) v(t) dt &= \int_0^\infty K(x, z) u(z) dz + \theta''' \bar{u}(A) \\ &= u(x) - v(x) + \theta''' \bar{u}(A) \end{aligned} \quad [12.16]$$

Since $\bar{u}(A) \rightarrow 0, A \rightarrow \infty$ by hypothesis, we have

$$u(x) = v(x) + \int_0^\infty K(x, t) v(t) dt = T^{-1}\{v(x)\} \quad [12.17]$$

Proofs of (2) and (3) of Theorem XX follow almost exactly by the same way as the corresponding portion of the Theorem IV of Part I and complement of Theorem IV of Part I

MAGNETIC ANISOTROPY AND PLEOCHROISM OF BIOTITE MICA.

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1 Introduction

THE micas constitute a highly interesting class of minerals on account of their characteristic crystalline structure and optical properties. Most varieties contain iron to a greater or less extent, in the combined state as well as in the form of inclusions, and as a result they are generally paramagnetic.¹ Biotite is distinguished by the presence in it of comparatively large amounts of iron, and its characteristic optical property is a strong pleochroism in the visible region of light. Light vibrations parallel to the cleavage plane are strongly absorbed, whereas vibrations normal to the plane are more or less freely transmitted. It is also well known that pleochroism is most marked in varieties rich in iron. The present investigation was undertaken in the hope that a study of the paramagnetic anisotropy, susceptibility and pleochroism of biotites of known composition might lead to interesting results regarding the nature and origin of these properties, while serving to throw light on the probable connection between pleochroism and magnetic anisotropy in paramagnetic solids.

The magnetic anisotropy of a large number of varieties of mica has been studied by E. Wilson.² He examined both spotted as well as clear varieties, and in all cases found that the paramagnetic susceptibility parallel to the cleavage plane was much greater than that perpendicular to it. The ratio $\frac{\chi_{\parallel}}{\chi_{\perp}}$ was very much greater in the spotted varieties. It was not clearly stated to which group the specimens belonged. Presumably only muscovite was examined. It was tentatively suggested that the anisotropy might be due to either an orderly arrangement of the inclusions of magnetite present, or an actual difference in the behaviour of the mica itself in different directions relative to the crystallographic axes. No attempt was made, however, to decide between the two hypotheses. The position has now altered considerably. Clear inclusion-free specimens of mica containing iron which forms an integral part of the lattice (as in phlogopite and biotite) may well show a

genuine crystalline magnetic anisotropy In the light of the X-ray crystallographic data now available³ and recent developments in the theory of the magnetic anisotropy of paramagnetic solids due to Van Vleck and Penney and Schlapp,⁴ a satisfactory interpretation of the magnetic data is now possible In the present investigation the author has determined the susceptibility and magnetic anisotropy of three varieties of biotite and one each of muscovite and phlogopite The ferrous and ferric iron contents of the specimens were determined by chemical analysis and the pleochroism of the specimens also estimated quantitatively

2 *Crystal Structure and Chemical Constitution of the Micas*

According to the recent theory developed by Van Vleck and Penney and Schlapp, the asymmetry of the strong crystalline electric fields acting on the paramagnetic ion is primarily responsible for magnetic anisotropy in paramagnetic solids These electric fields are due to the environment of anions or dipole molecules which are grouped around the cation The symmetry and nature of the grouping determines the character of the crystal fields and hence the magnetic anisotropy, in the case of any particular paramagnetic ion A knowledge of the exact disposition of the atoms in the crystal lattice is thus necessary for the interpretation of the magnetic data in the light of theory

The general scheme of the atomic structure of the micas was first elucidated by Pauling⁵ and the full investigation in the case of muscovite has been made by Jackson and West⁶ It has been shown that all the micas are built more or less according to the same plan The peculiar flaky structure and easy cleavage have been explained as being due to the formation of sheets of linked silicon-oxygen tetrahedra A sheet is formed by linking the oxygen atoms at the corners of the tetrahedra so that they are all in the same plane and the result is a hexagonal network Two such sheets placed with the vertices of the tetrahedra pointing inwards form a double sheet, the oxygen atoms at the vertices being cross-linked by aluminium atoms in muscovite, and magnesium and iron atoms in phlogopite and biotite Hydroxyl groups are incorporated, linked to Al, Mg or Fe alone We have thus a firmly bound double-sheet and the mica structure is a succession of such double-sheets interspaced alternately by sheets of potassium atoms The iron atoms occupy positions of six co-ordination and are surrounded by an octahedral grouping of oxygen atoms and hydroxyl groups X-ray evidence has shown that such a grouping is present in the hydrated sulphates and double-sulphates of iron, cobalt, nickel, etc, the water molecules in these salts constituting the octahedral environment The crystalline electric

fields due to such an arrangement are presumably of a highly asymmetric character as has been pointed out by Krishnan recently.

The chemical composition of the micas is variable within wide limits. Since the magnetic properties are determined by the iron content, as will be seen later, it is essential to know accurately the amount of iron present. In fact many properties of mica show a direct dependence on chemical composition. Kuntz⁷ has made a detailed study, combining optical and density determinations with chemical analysis. He established three series of isomorphous replacements and showed that the change in optical properties within one series depended mainly on the iron content. Similar classifications have been made by Hallmond, Winchell and Jakobs, and recently Niggli⁸ while discussing a recent paper by J. H. Linné on the crystal structure of biotite, has summarised the evidence from reliable chemical analysis and has pointed out the variability of the three types, *i.e.*, the muscovite type, the lithia mica type and the phlogopite-biotite type. A consideration of the physical properties in relation to chemical constitution shows that we cannot speak of a continuous transition from one group to another. This is probably due to the fact that the properties depend on the structure also besides chemical composition, and differences among the three types exist although the general plan of their architecture is similar. G. Nagelschmidt⁹ has recently found from an examination of the X-ray powder diagrams of eight different micas of known composition, density and optical properties, that they belong to at least two distinct types, the muscovite type and the phlogopite-biotite type. The lithia mica type could not, however, be distinguished.

The principles governing isomorphous substitution in the micas were established by the work of Mauguin¹⁰ who measured the dimensions of the unit cell in varieties of known density and composition. Ideal formulæ have been assigned based on such measurements, as follows:

Muscovite	$K Al_2 (AlSi_3O_{10}) (OH)_2$
Phlogopite	$K Mg_3 (AlSi_3O_{10}) (OH)_2$
Biotite	$K (Mg, Fe)_3 (AlSi_3O_{10}) (OH)_2$

3 Determination of Magnetic Anisotropy

The magnetic anisotropy has been measured by the torsional method developed by Krishnan¹¹. If an anisotropic crystal is suspended with one of its axes vertical by means of a fine quartz fibre in a uniform magnetic field, the forces acting upon it will be (1) a couple due to anisotropy of shape which will tend to rotate the crystal such that its length is along the field and (2) couple due to the magnetic anisotropy which will tend to rotate the crystal such that the direction of algebraically maximum susceptibility in the

horizontal plane is parallel to the field. Let us assume that (1) is negligible compared with (2). Let χ_{\max} and χ_{\min} be the maximum and minimum susceptibilities in the plane. If initially the torsion head of the fibre is adjusted that χ_{\max} is parallel to the field direction no couple acts on the crystal when the field is put on. If now the torsion head is turned round, the crystal also turns round but to a smaller extent on account of the couple due to magnetic anisotropy which begins to act on it when it leaves the zero position. At a critical position when χ_{\max} and χ_{\min} are making 45° with the field direction, this couple is a maximum and with the smallest further rotation of the torsion head the crystal will quickly turn round. If α_c is the angle through which the torsion head has been turned round, the specific anisotropy in the plane is given by the relation

$$\chi_{\max} - \chi_{\min} = 2 \left(\alpha_c - \frac{\pi}{4} \right) \frac{c}{m H^2}$$

where c is the torsional constant of the fibre, H the field strength and m the mass of the crystal. The micas crystallise on the monoclinic system and there are three principal susceptibilities of which two lie in the symmetry plane and the third along the symmetry axis. We have to determine the quantities $(\chi_1 - \chi_2)$, $(\chi_1 - \chi_3)$ and the relative orientation of the axes of the magnetic ellipsoid with respect to the crystallographic axes. χ_1 and χ_2 are the principal susceptibilities in the b (010) plane, χ_1 being nearer the a -axis and χ_2 is the principal susceptibility in the direction of the b -axis. The mica specimen was suspended in the uniform magnetic field as follows — (1) with the cleavage plane horizontal, (2) with the b -axis vertical and (3) with the b -axis horizontal and the cleavage plane vertical. We thus directly determine the quantities $(\chi_2 - \chi_a)$, $(\chi_1 - \chi_b)$ and $(\chi_2 - \chi_N)$ where χ_a is the susceptibility along the a -axis and χ_N is that perpendicular to the cleavage plane. From (2) we can directly get the angle which the χ_2 axis makes with the a -axis. This angle can also be calculated from the known values of $\chi_2 - \chi_N$ and $\chi_2 - \chi_a$, for,

$$\begin{aligned} \chi_2 - \chi_N &= \chi_2 - (\chi_2 \sin^2 \theta + \chi_1 \cos^2 \theta) \\ \chi_2 - \chi_a &= \chi_2 - (\chi_2 \cos^2 \theta + \chi_1 \sin^2 \theta) \end{aligned}$$

Solving the simultaneous equation we get both θ and $\chi_2 - \chi_1$. In the case of the micas matters are very much simplified, since the χ_2 direction was found to coincide with the direction of the a -axis.

4 Experimental Precautions and Sampling of Specimens for the Anisotropy Measurements

A careful selection of specimens for the magnetic determinations is absolutely essential, since inclusions and stains in mica are the rule rather

than the exception. Another serious difficulty in the case of rock minerals is that not only is the composition variable for varieties obtained from different localities but it might differ over different parts of the same specimen. The minerals are seldom perfectly homogeneous. For instance, inclusions may be very prominent in some regions of the same 'book' of mica, whereas other parts are clear and transparent. Often these inclusions consist of magnetite in dendrite-like forms. The presence of even small quantities of magnetite may be sufficient to cause considerable anomalies in the results. Other inclusions are, generally, flattened crystals of garnet, tourmaline and quartz in thin plates found between the sheets.

The micas were obtained in the form of small plates and of these the best were selected. These were further examined under a high power microscope and the portions containing included particles rejected. Satisfactory samples practically free from inclusions could be obtained. Inclusions in biotite are often associated with pleochroic haloes and afforded another test for their absence or presence. Phlogopite often shows asterism and this has been attributed to symmetrically arranged inclusions of rutile or tourmaline. Plates showing asterism were therefore rejected. In all cases, however, minute traces of inclusions mostly of submicroscopic dimensions were probably present.

The optical characteristics of the specimens were also examined under the polarising microscope. With convergent polarised light the muscovite specimens gave the usual biaxial interference figure, whereas the phlogopite and the biotite samples were sensibly uniaxial. No evidence of twinning was found in the plates taken up for examination. The optical axial plane is perpendicular to the b (010) plane in muscovite and parallel to the b (010) in phlogopite and biotite.

Only freshly cleaved plates were employed. These were further cleaned with dilute sulphuric acid, distilled water and alcohol.

In the case of mica, which was available in the form of thin plates only, we cannot neglect the effect due to the anisotropy of shape of the specimen. For the paramagnetic susceptibility is fairly high, especially in the case of the biotites, and in some cases the magnetic anisotropy also is comparatively small. The possible errors on this account were eliminated by adopting the device of Krishnan of immersing the crystal in a liquid bath of the same mean susceptibility, for phlogopite and muscovite. An aqueous solution of manganese chloride was employed. For determining the anisotropy in the cleavage plane, which was found to be very feeble, discs of the material 5.5 mm in diameter were prepared. In this case no correction for anisotropy of shape is necessary.

For the biotites the paramagnetic susceptibility was too high for a liquid-bath to be employed conveniently. Small plates 1 cm by 4 mm were cut out, cleaned with dilute acid and distilled water and placed one above the other to form a block $10 \times 4 \times 4$ mm using traces of diamagnetic shellac for attaching them. Particular care was taken to see that the crystallographic directions of the plates coincided when cutting them out. The long edges were carefully rounded off so that a cylinder, 10 mm height and 4 mm diameter, was obtained. A silk thread was further wound round the cylinder so that the pieces might not fall off. It was finally cleaned with dilute sulphuric acid and distilled water. For determining the magnetic anisotropy in the cleavage plane discs 5.5 mm in diameter were used. Only the value of $\chi_{\parallel} - \chi_{\perp}$ is given for biotite and phlogopite since the anisotropy in the cleavage plane was negligibly small.

The current through the electromagnet was adjusted by the use of a system of rheostats, and every time before the field was applied the iron was brought to a cyclic state by reversing the current several times. Uniformity of field over a large area was ensured by using flat pole-pieces of area 50 sq cm nearly.

The field strength was measured by means of a calibrated Grassot flux-meter and a standard search coil made by the author consisting of 30 turns of No. 40 s.w.g. double silk-covered copper wire wound round an accurately turned cylinder of non-magnetic marble, the diameter of the coil being 2.359 cm. Fields of the order of 1000–2000 oersteds were employed.

For mounting the crystal a thin glass fibre 1.5 cm long and shaped like a pin was attached to the end of the quartz fibre with the pin-head down. The mica pieces were fixed to the pin-head by traces of pure shellac.

The torsional constant of the fibre was determined by suspending at its end a glass cylinder 0.327 cm diameter and mass 0.0998 g with its axis vertical and observing the period of oscillation, by the usual methods.

The mean of several independent determinations is given in Table I.

5 *Measurement of Absolute Susceptibilities*

The mean susceptibility of the micas in the form of powder was determined by the Curie-Balance method. A torsion balance of the Curie-Wilson type was constructed by the author with a glass beam and glass extensions for supporting the phial holding the substance, all made of pyrex. A schematic diagram of the balance is shown in Fig. 1. The inhomogeneous magnetic field was obtained by keeping the pole pieces (specially designed by the author to go with an electromagnet made by Charles W. Cook & Son, Ashby de la Zouch) at an angle to each other. As is well known the

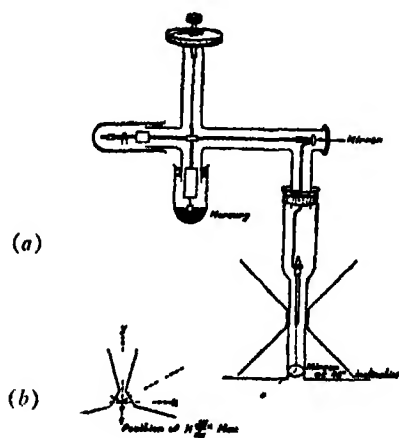


FIG 1

susceptibility is given by the formula

$$\chi = \frac{1}{m} \left\{ \chi' m' + (\chi'' m'' - \chi' m') \left(\frac{F_{x2} - F_{x1}}{F_{x3} - F_{x1}} \right) \right\},$$

where χ , m represent the susceptibility and mass of the specimen, χ' , m' of the air and χ'' , m'' of the standard substance respectively, the masses referring to equal volumes of the substances

F_{x1} the force acting on the container alone measured by the torque on the torsion wire,

F_{x2} the force acting on the phial + substance, and

F_{x3} the force acting on the phial + standard substance

All the usual precautions were taken, the most important being that the container is always brought back to the same position relative to the field when taking the measurements, and that the field is kept constant. The standard substances used was a solution of manganese chloride (33.8%) the susceptibility of which was accurately determined by the Quincke U-tube method.

6 Determination of Ferrous and Ferric Iron in the Specimens

The percentage of total iron and ferrous iron in the micas were determined by the following methods¹²

Total Iron—The sample was ground to a fine powder in an agate mortar, and about 0.5 g of the powder weighed in a platinum crucible and then fused with fusion mixture (two parts of Na_2CO_3 and one part of K_2CO_3). The fused mass after cooling was dissolved in dilute HCl in a silica dish, evaporated to dryness over a water-bath, redissolved in dilute HCl and the

silica filtered off, washed on the filter and weighed after ignition. The filtrate was heated up to boiling point and a little concentrated nitric acid added followed by 20 g of ammonium chloride. Ammonia was then slowly added to the boiling solution until all the aluminium and iron were precipitated as hydroxide and the solution became slightly alkaline. The precipitate was then filtered off, washed on the filter with a warm solution of ammonium nitrate and ignited in a platinum crucible and weighed. The ignited mass was then fused with sodium bisulphate and after cooling dissolved in dilute sulphuric acid. The solution was then run through a Jones' reductor (an improved form of which has been devised by the author and reported elsewhere) in an atmosphere of carbon dioxide and finally titrated against standard permanganate.

Ferrous Iron —The accurate determination of ferrous iron in silicate rocks is a matter of considerable difficulty. The modified Pratt method recommended by Hillebrand was adopted. A weighed quantity of mica was carefully ground in an agate mortar under pure alcohol for about an hour. A thorough grinding is necessary since coarse particles take a very long time to get dissolved in HCl . The ground mass was carefully washed down into a platinum crucible with air-free water and 10 c.c. of cold dilute sulphuric acid added. The crucible was supported over a water bath and surrounded by an atmosphere of CO_2 by the arrangement shown in Fig. 2. 6 c.c. of

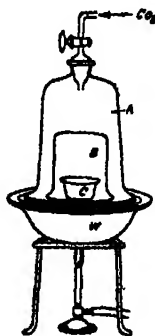


FIG. 2

A —Bell-jar, *B* —Beaker, *C* —Platinum crucible, *W* —Water-bath

40% hydrofluoric acid (Kahlbaum's analytical reagent) were quickly introduced into the crucible which was then covered with the lid and the water-bath heated, carbon dioxide being passed all the time. The reaction was allowed to go on for 3 hours. Meanwhile a solution containing 50 g of boric acid and 20 c.c. of sulphuric acid in 300 c.c. of air-free water was prepared and the crucible and contents, after the reaction was over,

were quickly transferred into the cold boric acid solution and titrated immediately against standard permanganate, until a pink colour lasting for a minute or two was obtained

A blank experiment was performed under similar conditions with ferrous ammonium sulphate. About 0.5 g was weighed and dissolved in 300 c.c. of dilute sulphuric acid and immediately titrated against permanganate. Another 0.5 g was weighed in a platinum crucible and the ferrous iron determined by the modified Pratt method as described above, using 6 c.c. of HF. The necessary correction was found to be + 0.28 c.c. of permanganate.

7 Measurement of the Pleochroism of the Micas

A comparative measure of the pleochroism of the micas was obtained by the following experimental arrangement based on the principle of Cornu's method for determining the percentage of polarised light (Fig. 3)



FIG. 3

S.—Source of light, TS—Translucent Screen, Sp—Specimen,
SI—Rectangular slit, DIP—Double-Image prism,
N—Nicol mounted on circular scale, T—Telemicroscope

The specimens were used in the form of thin plates, freshly cleaved, and of the same thickness 0.05 mm, selected from a very large number of cleaved plates. The mica plates were mounted behind the slit at an angle of 45° with the *b*-axes horizontal. The double image prism was placed with the vibration directions vertical and horizontal, and the distance from the slit was adjusted until the two images, as seen through the telemicroscope, just touched one another. The horizontal vibrations are absorbed much more than the vertical and the images are of unequal intensity. By suitably rotating the nicol the intensities can be equalised. If 2θ is the angle between two positions of the nicol on either side of the vertical for which the intensities are equalised, then $\frac{I_v}{I_H} = \tan^2 \theta$. A correction has to be introduced in the value of θ to eliminate errors due to reflection, etc., at the faces of the plates. For this a blank experiment was performed with a glass microscope coverslip of nearly the same refractive index as the mica plates and the necessary correction applied to the value of θ . The results are approximate only but afford a good comparative measure of the pleochroism of the micas.

The corrected values of $\tan^2 \theta$ are given in Table III

8 Results

The results are presented in the tables shown below

TABLE I *Specific Magnetic Anisotropy of Phlogopite and Biotite*
C G S E M Units Temperature 25° C

Specimen	Anisotropy $\chi_{\parallel} - \chi_{\perp}$ $\times 10^6$	Remarks
Phlogopite .	1 38	The magnetic anisotropy in the cleavage plane was negligibly small in all cases and, therefore, only the values of $\chi_{\parallel} - \chi_{\perp}$ are given
Biotite (Canada) .	6 25	
„ (Ural Mts)	10 3	
„ (Bihar)	12 4	

Specific Magnetic Anisotropy of Muscovite

Mode of Suspension	Orientation	Anisotropy $\Delta \chi \times 10^6$	Remarks
Cleavage plane horizontal	<i>b</i> -Axis perpendicular to the field	$\chi_2 - \chi_3 = 0.11$	The χ_3 direction coincides with the <i>a</i> -axis
<i>b</i> -Axis vertical	Cleavage plane parallel to the field	$\chi_2 - \chi_1 = 0.70$	
<i>b</i> -Axis horizontal and cleavage plane vertical	Do.	$\chi_3 - \chi_1 = 0.61$	

TABLE II *Mean Susceptibility of the Micas at 25° C.*

Specimen	$\bar{\chi} \times 10^6$
Muscovite	8.01
Phlogopite	7.85
Biotite (Canada)	30.8
„ (Ural Mts) .	40.6
„ (Bihar)	43.8

TABLE III
Pleochroism of the Micas

Specimens of thickness 0.05 mm	$\tan^2 \theta = \frac{I_v}{I_h}$
Muscovite	1.03
Phlogopite	1.09
Biotite (Canada)	1.58
„ (Ural Mts)	1.89
„ (Bihar)	1.97

TABLE IV
C G S E M Units Temperature 25° C

Specimen, Description (Colour of the Biotites refers to very thin plates)	Mean Susceptibility $\chi \times 10^6$	Magnetic Anisotropy $\chi_{ } - \chi_{\perp} \times 10^6$	$\chi_{ } \times 10^6$	$\chi_{\perp} \times 10^6$	Total Iron %	Ferrous Iron %	Ferric Iron %	Magnetic Anisotropy referred to a g ion of $\text{Fe}^{++} \times 10^6$
Muscovite Clear. Tinge of green	8.01	0.65	8.23	7.58	3.93	1.79	2.14	
Phlogopite Brownish yellow Submetallic lustre	7.85	1.38	8.31	6.93	4.34	3.18	1.06	2420
Biotite (Canada) Dark greenish brown	30.8	6.25	32.9	26.6	15.2	13.1	2.12	2670
Biotite (Ural Mts) Dark brown	40.6	10.3	44.0	33.7	21.8	19.6	2.22	2930
Biotite (Bihar) Dark reddish brown	43.8	12.4	47.8	35.4	23.1	22.2	0.9	3120

9. Discussion of Results.

Both the susceptibility and the magnetic anisotropy are seen to depend upon the amount of iron present. The biotites exhibit a fairly large magnetic anisotropy and the paramagnetic susceptibility is also correspondingly high. The values for muscovite and phlogopite are comparatively small. In the case of the biotites the mean susceptibility is seen to increase with the percentage of iron almost linearly (Fig 4)

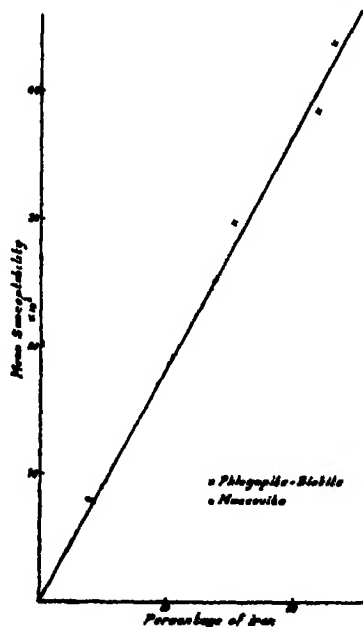


FIG 4.

The total susceptibility of mica may be considered to consist of three parts, namely (1) that due to the ferrous iron, (2) that due to the ferric iron and (3) the contribution due to the other atoms. The first two are evidently paramagnetic terms while the last is diamagnetic. When the percentage of iron is large, as obtains in the case of the biotites, the diamagnetic term will be negligibly small as compared with the paramagnetic terms. But it will be considerable in muscovite and phlogopite which contain only about 4% of iron.

It will be of interest to calculate in a rough way the approximate Bohr magneton values for the biotites. The susceptibility of the biotites is amenable to theoretical considerations for the following reasons: (1) The percentage of iron is very high and we may neglect the diamagnetic term in the susceptibility; (2) Most of the

iron is present in the ferrous state, (3) The disturbing effects due to possible minute traces of inclusions can be safely ignored (In fact, the biotite samples were particularly free from defects) Considering only the total iron present, the effective Bohr magneton value is obtained according to the formula $P_{B \text{ eff}} = 2.84 \sqrt{X_M} T$

	$P_{B \text{ eff}}$
Biotite (Canada)	= 5.2
„ (Ural Mts.)	= 5.0
„ (Bihar)	= 5.0

The values are seen to be much lower than the theoretical values to be expected in the case of the free paramagnetic ion just as in the case of other solid salts of iron. They are found to approach the spin only value of Fe^{II} , which is equal to 4.92 Bohr magnetons. The significance of this fact in the light of Van Vleck's theory of the quenching of the orbital moments by the crystalline electric fields in paramagnetic solids will be discussed later.

It is important to consider the effect of microscopic and submicroscopic inclusions on the magnetic anisotropy, especially in the case of muscovite which, according to the ideal formula $KAl_2(AlSi_3O_{10})(OH)_2$, cannot take in ferrous iron in the positions of six co-ordination replacing the aluminium atoms. We have to see if the magnetic anisotropy of muscovite is merely due to symmetrically arranged inclusions or if it can be of crystalline origin as in biotite, at least in part. If according to the ideal formula, the ferrous iron cannot form an integral part of the lattice, then apparently we are led to conclude that only the inclusions, microscopic or submicroscopic, are responsible for the anisotropy. But chemical analysis shows that very often the amount of ferrous iron present is much larger than can be accounted for by any of the common inclusions. For instance, in the muscovite sample examined by the author which contained inclusions of magnetite, the percentage of FeO is much larger than should be expected. The ferrous iron, therefore, is most probably present in the mica lattice itself in the positions of six co-ordination. The iron atoms should be present in groups to satisfy the rules of co-ordination and as such they really constitute a discontinuity in the lattice. We may regard them as being of the nature of inclusions of extremely small dimensions. This view gains support from the fact that biotite inclusions in muscovite are often met with and from what we know of the crystal structure of the micas a biotite inclusion can really be regarded as a discontinuity of the above character occurring over an extended region, magnesium also being present along with the iron in the positions of six co-ordination. Thus the anisotropy measurements throw an interesting sidelight and seem to provide evidence for the presence of discontinuities in the

lattice which cannot be detected by the microscope. The effect of inclusions on the magnetic anisotropy of the biotites will be comparatively negligible since, on one hand they are much less prominent and on the other the iron forming part of the lattice is present in very large amounts.

The close correspondence between the magnetic properties of the micas and their structure is very striking. In muscovite, as is to be expected from its pseudo-hexagonal structure, two of the principal susceptibilities lie in the cleavage plane and are nearly equal, while the susceptibility perpendicular to the plane is much less than either of the other two. In biotite and phlogopite two of the principal susceptibilities not only lie in the cleavage plane but are also of the same value. It must be emphasised, however, that the determination of the magnetic anisotropy in the cleavage plane was complicated by two factors namely, (1) strains and distortions set up when cutting out the specimens in the shape of discs and (2) the presence of microscopic inclusions. The spurious effects due to the first cause could be eliminated by exercising proper care in the preparation of the discs. The effect due to the second cause was studied by determining the magnetic anisotropy in the cleavage plane of a large number of spotted and stained samples of muscovite. The heavily spotted varieties always showed enormous anisotropy in the cleavage plane while those with perceptible traces of inclusions (magnetite) were anisotropic to the extent to which they contained the inclusions and this was considerable.

From the results it could be inferred that the contribution due to the minute traces of inclusion should be much less than the observed anisotropy in the cleavage plane, and that at least part of the observed anisotropy in the cleavage plane is genuine. The definite orientation of the b axis in the magnetic field in all cases also leads to the same conclusion. In this connection the isotropy of phlogopite and the biotites in the cleavage plane is interesting. It proves that the disturbing effects due to any inclusions present are negligible. Samples of phlogopite which exhibited marked asterism showed considerable anisotropy in the cleavage plane. There is a close similarity between the optical and magnetic properties also, when we remember that the muscovite showed a biaxial interference figure whereas the phlogopite and the biotites were sensibly uniaxial.

Magnetic Anisotropy and Chemical Constitution —The specific magnetic anisotropy is plotted as a function of the total iron, ferrous iron and ferric iron respectively in Fig. 5. Since phlogopite and biotite belong to the same group we can study the characteristics of this group from the results obtained. In the first place there seems to be no obvious connection between

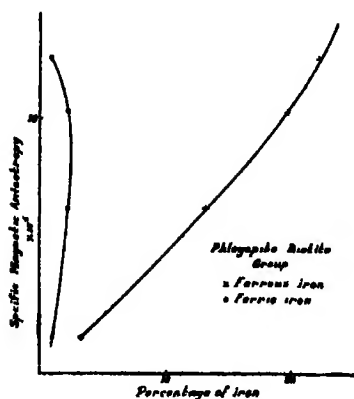


FIG 5

the ferric iron content and the anisotropy. On the other hand, the magnetic anisotropy increases smoothly with the percentage of ferrous iron. But the relationship is not linear and for large percentages of iron the curve becomes steeper. In Table IV the gram ionic anisotropy for Fe^{+2} is given. This shows a remarkable increase with the percentage of ferrous iron in the biotites (Fig 6). It is likely that this increase is due to interaction between

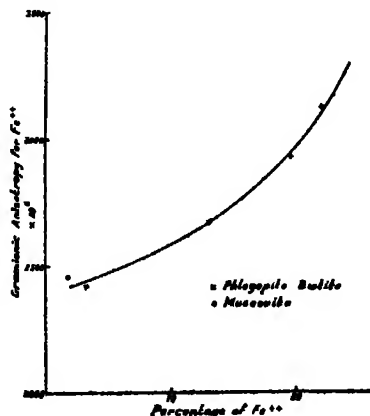


FIG. 6.

neighbouring iron atoms in the sheet. The nature of this interaction will be discussed later.

The results obtained are significant in the light of recent theoretical developments due to Van Vleck and Penney and Schlapp.

Van Vleck's Theory of the Paramagnetism of Solids—The object of the theory is to account for the following features in the magnetic behaviour of paramagnetic solids, such as (1) the departure from the Curie law and the

appearance of cryomagnetic anomalies at low temperatures, (2) the relative contributions of the spin and orbital moments to the susceptibility and (3) the magnetic anisotropy of the crystals. It is based on the earlier work of Bethe and Kramers on the Stark splitting of the energy levels of atoms and ions under the influence of crystalline electric fields. Detailed computations have been made by Penney and Schlapp, who have considered Pr and Nd among the rare earths and Co, Cr and Ni in the iron group. Jordahl has made calculations in the case of the cupric salts. The main results for the salts of the iron group are as follows. Since the magnetically effective 3d electrons are in the outermost shell, the influence of the crystalline electric fields due to the neighbouring atoms will be strong enough to break the coupling between the orbital and spin moments. The orbital degeneracy is partially or completely removed and the orbital moment makes practically no contribution to the susceptibility. The orbital moment is then said to be quenched. The spins, however, are not directly affected by the crystalline fields and hence contribute fully to the susceptibility. An asymmetric crystalline field produces asymmetric partial freezing of the orbital moment and due to the coupling between orbit and spin, since the remnants of the orbital moment are anisotropic, the freedom of the spins to orient themselves along different directions will be different. Hence the crystal exhibits magnetic anisotropy. Due to the partial quenching of the orbital moments the susceptibility lies between the limits given by $P_B' = \sqrt{4S(S+1)}$ and $P_B' = \sqrt{4S(S+1) + L(L+1)}$. In fact we have pointed out earlier that in the case of the biotites this is the case, the Bohr magneton values approaching the spin only value. One important consequence of Van Vleck's theory is that manganous and ferric salts should not exhibit any marked anisotropy, since the Mn^{++} and Fe^{++} ions are in the S state and therefore have no orbital moment to be quenched. The present investigation also shows how the magnetic anisotropy of biotite is not dependent on the amount of ferric iron in the specimens, and thus lends support to the theory.

In many hydrated paramagnetic crystals which exhibit large magnetic anisotropy, there is evidence from X-ray analysis that we have an octahedral arrangement of water molecules round the paramagnetic ion. Recent experimental work shows that the crystalline electric field due to such an arrangement deviates widely from cubic symmetry¹⁸ and most probably possesses only hexagonal symmetry. Usually in such paramagnetic crystals there are a number of these complexes (formed by the paramagnetic ion and its environment of six water molecules) in the unit cell, differently oriented with respect to each other, such that crystalline magnetic properties may have only the lower rhombic symmetry. But in the micas the case is much

simpler Here the octahedral group around the Fe^{++} ion consists of four oxygen atoms and two hydroxyl groups and all the groups are arranged parallel to each other in layers in the crystal lattice Hence the anisotropy of the crystal actually corresponds to that of these individual paramagnetic complexes The hexagonal symmetry of phlogopite and biotite as regards the magnetic properties lends support to the view that the crystalline electric fields due to the octahedral grouping possess the same symmetry In the case of muscovite, however, the departure from hexagonal symmetry may be attributed to the staggering of the sheets relative to each other which is responsible for the monoclinic angle of 95° and which probably introduces slight departures from the octahedral symmetry of the environment round the Fe^{++} ion Since the 3d electrons occupy the outer shell they are very susceptible to slight changes in the positions of the surrounding atoms which can cause considerable variation in the character of the crystalline fields influencing these outer electrons The magnetic anisotropy of the paramagnetic complex $[(\text{Fe}(\text{OH})_6)]$ referred to a gram ion is most probably the value obtained for phlogopite since, here, the magnetic dilution is large enough for the interaction due to neighbouring paramagnetic atoms to be ignored

The rapid increase in the magnetic anisotropy of the biotites with the percentage of iron is a new feature and gives an insight into the effect of the concentration of the paramagnetic ion on the magnetic anisotropy The explanation in this case seems to be that it is due to the interaction between neighbouring iron atoms The peculiar structure of mica is very favourable for such interaction to take place since the iron atoms lie all in the same plane and their population is sufficiently high in the biotites for most of them to occupy neighbouring positions of six co-ordination Interactions of this character are not taken into account by Van Vleck's theory which is strictly applicable only in the case of salts of considerable magnetic dilution, *e.g.*, the highly hydrated sulphates and double sulphates of the transition elements

These interactions are the 'exchange effects' or 'Austausch' discovered by Heisenberg The exchange effects are formally equivalent to a strong coupling between the spins of the interacting electrons and take place when the interatomic distance has a critical value in ferromagnetics ($2.7-3 \text{ \AA}$ according to Forrer, in the case of iron) In the biotites, however, the distance between positions of six co-ordination is of the order of 2.6 \AA which is less than this critical value For explaining the experimental results it is enough to assume that the effect of these interactions is equivalent to imposing a further restriction on the freedom of orientation of the orbital moments This will naturally increase the magnetic anisotropy At the

same time we should expect a decrease in the Bohr magneton value due to the further quenching of the orbital moments. This is actually found to be the case, for we find that with the increase in the percentage of iron there is a corresponding decrease in the approximate effective Bohr magneton value. Thus the explanation offered seems to be quite satisfactory although the exact nature of the interaction has to be investigated further.

10 *Pleochroism of the Biotites*

There is, as yet, no satisfactory explanation of the pleochroism of the biotites. The intimate relationship between colours of inorganic salts and paramagnetism is well known, for salts of the transition elements which are coloured are also paramagnetic. Saha¹⁴ has put forward a theory of the origin of colour in inorganic salts according to which absorption in the visible region of light is due to transitions involving the reversal of the spin vector of the one of the 3d electrons of the paramagnetic ion. Such transitions although forbidden for the free paramagnetic ion are assumed to be possible in solids and in solutions. Subsequent work by Bose and others lends support to this view.

The connection between colour and paramagnetism at once suggests a corresponding relationship between pleochroism and paramagnetic anisotropy and the examination by the author of the available data on the pleochroism and paramagnetic anisotropy of salts of the iron group of elements has revealed that strong paramagnetic anisotropy is generally associated with marked pleochroism. This enquiry proved to be fruitful in another way. The author could not find any reference to the pleochroic properties of $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ in the literature on the subject. This substance is known to be highly anisotropic magnetically and we should expect a marked pleochroism also. A large single crystal was examined in the (010) plane and it was found that the colour is pale green for light vibrations in the γ direction and yellow when the vibrations are in the α direction.

The bearing of the above on the pleochroism of the biotites is obvious, for we have seen that pleochroism is most pronounced in the varieties rich in ferrous iron and the magnetic anisotropy also increases with the iron content. The two phenomena are evidently closely related. If the mechanism of absorption of light in biotite by the iron atom is the same as suggested by Saha (The positions of the absorption maxima are slightly different in the different specimens and seem to correspond roughly with the $^6\text{D} - ^4\text{P}$ and $^6\text{D} - ^4\text{F}$ transitions for Fe^{2+}) the pleochroism implies that the reversal of the spin vector can take place only when the light vibrations are parallel to the cleavage plane and not when they are perpendicular. This

restriction in the orientation of the spins is evidently due to the influence of the asymmetric crystalline fields which, according to Van Vleck, act indirectly on the spins through the spin orbit coupling and which are responsible for the large magnetic anisotropy

The close correspondence between the ease of magnetisation parallel to the cleavage plane (the paramagnetic susceptibility parallel to the cleavage plane is much greater than that perpendicular to it) and the readiness with which the spins respond to the electric field of light wave when this is parallel to the cleavage plane is very striking and is strongly suggestive of the fact that the polarisation of absorption in the biotites is chiefly due to the influence of the asymmetric crystalline fields acting on the paramagnetic ion enhanced, however, by the spin-spin interactions. The recent work of Krishnan and Chakrabarty¹⁸ on the polarisation of the absorption lines of single crystals of the hydrated sulphates of Pr and Nd is interesting in this connection. They find that "many of the absorption lines are strongly polarised, some of them being confined almost wholly to vibrations along one or another of the principal axes of the optical ellipsoid of the crystal and that these variations in the direction of polarisation occur even among the lines of the same group, in other words, among the Stark components which originate from the same absorption line of the free ion, some are polarised strongly in one direction and some strongly in another". These crystals also show strong magnetic anisotropy. From these facts Krishnan concludes that the crystalline electric fields which produce the Stark splitting are also highly anisotropic.

The nature and disposition of the magnetic carriers in biotite may now be understood from the following picture. The orbital moments being mostly frozen, the freedom of orientation of the spins is also restricted considerably. We assume that the spins are mostly oriented with the magnetic axes nearly parallel to the cleavage plane, randomness of orientation existing in azimuth, so that there is no residual magnetisation as should be the case in paramagnetics. The magnetic carriers possess complete freedom of orientation in the cleavage plane. Under the influence of a magnetic field parallel to the cleavage plane, we get the usual paramagnetism although considerably diminished in magnitude. But when the field is normal to the cleavage plane, the resolved part of the spin moments perpendicular to the cleavage plane is much less on account of the restrictive action of the crystal fields, and we get a much lower susceptibility. Thus the high magnetic anisotropy may be explained. Our picture also reveals how the reversal of the spin vector can take place in the cleavage plane but not perpendicular to it since the spins are directed more or less parallel to

the cleavage plane. The pleochroism also is thus satisfactorily explained. This physical picture although somewhat naive is sufficient to explain both phenomena in a crude way. A rigorous treatment of pleochroism taking into account the Stark splitting of the energy levels in the crystal fields is very desirable.

It seems very likely that the mutual interaction of neighbouring paramagnetic ions, to which we ascribed the enhanced anisotropy in the varieties rich in iron, plays a significant part in intensifying the pleochroism, although at present we cannot say to what extent. But it is seen that when the percentage of ferrous iron exceeds a certain value, the effect due to the interaction of the iron atoms may become enormous as compared with the usual Van Vleck effect of the asymmetric fields, and both the magnetic anisotropy and the pleochroism become exceedingly large.

Although the connection between pleochroism and paramagnetic anisotropy seems to be obvious in the biotites, further quantitative investigation is necessary in the case of other paramagnetic salts to establish the generality of the relationship. Some anomalous features also have to be explained. For instance, Murmann and Rotter have observed pleochroism in $\text{MnSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ ¹⁶ although this crystal is almost isotropic magnetically. Again in the case of a rose-coloured variety of tourmaline containing a considerable percentage of manganese the author has observed pronounced pleochroism, the absorption band in green being very strongly polarised, while the magnetic anisotropy is very feeble. The crystal is paramagnetic. $\chi = 0.31 \times 10^{-6}$, $\chi_{\perp} - \chi_{\parallel} = 0.008 \times 10^{-6}$ cgs E.M. units. This would indicate that at least as regards relative magnitudes, in all cases, pleochroism and magnetic anisotropy bear no simple relationship to each other.

A quantitative study of the polarisation of the absorption bands of paramagnetic crystals of salts of the iron group of elements, in relation to their magnetic anisotropy is under progress in order to further elucidate the connection between the two phenomena.

My heartfelt thanks are due to Sir C. V. Raman, F.R.S., N.I., for suggesting the problem and for his encouragement and helpful criticism. I also wish to express my indebtedness to Mr. N. Jayaraman for his assistance while doing the chemical analysis and to Dr. K. R. Krishnaswami, D.Sc., for kindly providing me with facilities for the same.

Summary

The paramagnetic anisotropy and susceptibility of three different varieties of biotite and one each of muscovite and phlogopite have been

determined. The ferrous and ferric iron contents of the specimens have also been found by chemical analysis and their pleochroism estimated quantitatively. It is found that the biotites are highly anisotropic and that both the anisotropy and the pleochroism increase with the iron content. The magnetic anisotropy is seen to depend only on the amount of ferrous iron and not on the ferric iron. The relationship between the gram ionic anisotropy referred to Fe^{++} , and the percentage of iron is not linear when the latter is high. The anisotropy, in fact, increases more rapidly and this is attributed to the mutual interactions of neighbouring paramagnetic atoms, which cannot be neglected for high concentrations of the latter. The results, in general, are in agreement with the theory of the paramagnetism of solids recently developed by Van Vleck and Penney and Schlapp based on the Stark splitting of the energy levels of the paramagnetic ion under the influence of the strong asymmetric crystalline electric fields. The pleochroism of biotite is discussed in the light of Saha's view that absorption of light in inorganic salts of elements of the transition series is due to transitions involving the reversal of the spin vector of one of the 3d electrons of the cation. In biotite where the absorption is essentially due to the ferrous iron, the pleochroism is explained as being due to the fact that the reversal of the spin vector of the 3d electrons of the Fe^{++} ion can take place only when the light vibrations are parallel to the cleavage plane. This restriction on the spins is attributed to the influence of the asymmetric crystalline fields which according to Van Vleck's theory give rise to the magnetic anisotropy also. This affords a satisfactory theoretical explanation of the origin of pleochroism besides indicating the character of its intimate relationship with paramagnetic anisotropy, observed experimentally.

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A STUDY OF THE BENZOIN REACTION.

VI. The Effect of Temperature Variation on the Benzoïn Reaction

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Received July 22, 1938

FOR some time past this Laboratory has been engaged on a study of the kinetics of the benzoïn reaction between solid potassium cyanide and benzaldehyde¹. It has been shown that when pure potassium cyanide and pure benzaldehyde react, two concurrent reactions take place—a fast homogeneous autocatalytic reaction, between benzaldehyde and a trace of potassium cyanide dissolved in it, which requires the presence of benzoïn, and a slow heterogeneous reaction between benzaldehyde and the solid potassium cyanide. The slow heterogeneous reaction is subject to inhibition by compounds such as potassium chloride, iodine and quinone. This paper comprises a study of the effect of temperature variation between 60° C and 120° C on the two reactions involved, previous work has been done at 100° C.

Experimental Technique and Discussion of Results

The analytical methods and the general technique have been described in the previous papers. Merck's purest benzaldehyde, pretreated with potassium cyanide (Part V, *loc cit*, p 614) and Kahlbaum's purest potassium cyanide dried at 110° C at 2 mm pressure for 2 hours were used. Water was employed in the thermostat up to 100° C and above that glycerol. The temperature was kept constant to within 0.3° C.

The approximate solubility of benzoïn in benzaldehyde was determined as it was required in the examination of the results. The method employed involved observation of the clouding-points of benzoïn solutions of known strength in benzaldehyde. Table I summarises the solubility results.

Figs 1, 2 and 3 give the experimental observations on the production of benzoïn. It will be seen that the time-yield curves are of the same type as those previously obtained at 100° C. Above 100° C it is difficult to follow the reaction owing to its rapidity and there is evidence of the decomposition

¹ Parts I, II and III, *J. Physical Chem.*, 1935, 39, 727, 901, 907, Parts IV and V, *Proc. Ind. Acad. Sci., (A)*, 1935, 2, 483, 605.

TABLE I

Temperature ° C	G benzoin dissolved in 10 g benzaldehyde
60	2 6
70	4 0
80	5 8
90	8 0
100	10 6

Above 100° C miscibility is rapidly obtained of the benzoin formed by the further action of potassium cyanide. A similar effect was observed by Lachman.²

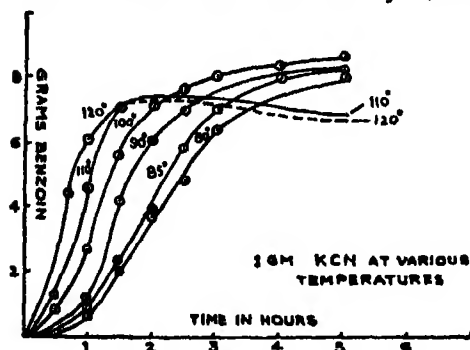


Fig 1

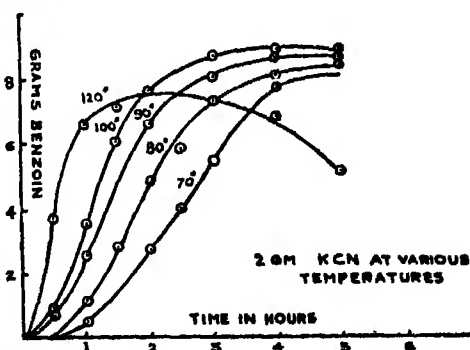


Fig 2

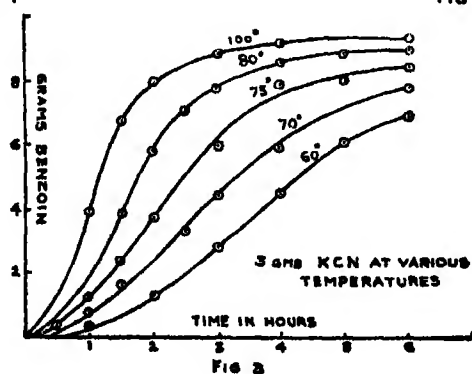


Fig 3

² J. Amer. Chem. Soc., 1924, 46, 710

A mathematical study of the results shows that the equation which was worked out in Part I for the initial stages of the reaction up to the separation of benzoin can here be applied. The equation is —

$$t - c' = -1/k_1 [-5/n' + 3.45 \log n' - 4.60 \log (10 + X' - n')]$$

where $n' = g$ benzaldehyde remaining at time t ,

k_1 = the value of the homogeneous constant,

$X' = 2k'_2/k_1$, k'_2 being the heterogeneous constant,

and c' is a constant

At 100°, k'_2 for 1 g effective KCN per 10 g benzaldehyde is 0.185, and k_1 is 5.7. Effective KCN, it may be noted, is the gross quantity of KCN used less 0.17 g, since it has been found previously (Part I, p. 730) that 0.17 g KCN is always ineffective in the experiments. Further experiments have shown that at higher temperatures the inactivity of this small amount of cyanide still persists.

On investigating the application of the above equation, it was found that between 80° C and 100° C and possibly up to 120° C, k_1 the homogeneous constant does not change, but retains the value 5.7.

The heterogeneous constant k_2 is found in the range involved to be approximately doubled for each rise in temperature of 10° C, this ratio for the temperature coefficient is not unusual. Stern³ found a similar temperature coefficient for the reaction in aqueous alcoholic solution. We can accordingly write the equation for the temperature range investigated as given above putting k_2 for 1 g of effective KCN per 10 g benzaldehyde equal to $0.185 \times 2^{\frac{\theta - 100}{10}}$, θ being expressed in °C.

Table II shows the value of X' for the various series of experiments made in the present investigation. By choosing suitable values of c' it was found possible to reproduce all the experimental curves obtained between 80° C and 100° C up to approximately the point at which from the results given in Table I, benzoin was known to be separating.

At 110° C and 120° C there is decomposition of benzoin, but the initial portions of the curves for 1 g KCN at 110° C and 120° C could be reproduced by the same equation. Below 80° C the regularities in the values of k_1 and k'_2 were no longer to be observed, both appeared to decrease in value with further reduction in temperature.

³ *Z. physikal. Chem.*, 1905, 50, 554

TABLE II

Temperature ° C	KCN used (a) g.	KCN effective (b = a - 0.17) g	$k_2' = 0.185 b$ $\frac{\theta - 100}{10}$ $\times 2$	$X' = \frac{2k_2'}{5.7}$
80	1.0	0.83	0.038	0.013
80	2.0	1.83	0.085	0.030
80	3.0	2.83	0.131	0.046
85	1.0	0.83	0.054	0.019
90	1.0	0.83	0.077	0.027
90	2.0	1.83	0.169	0.059
100	1.0	0.83	0.154	0.054
100	2.0	1.83	0.338	0.119
100	3.0	2.83	0.524	0.184
110	1.0	0.83	0.307	0.108
120	1.0	0.83	0.614	0.216

Summary

Continuation of the investigation of the benzoin reaction between pure potassium cyanide and pure benzaldehyde in the absence of solvents and diluents has shown that between 80°C and 110°C the rate of the fast homogeneous autocatalytic reaction remains unaltered, the slow heterogeneous reaction has its rate approximately doubled for each 10°C rise in temperature.

DIFFRACTION OF X-RAYS IN ORGANIC GLASSES.

BY T M K NEDUNGADI

Received August 15, 1938

(Communicated by Sir C V Raman, Kt, FRS, NI)

Introduction

X-RAY diffraction studies with glasses have greatly assisted in elucidating the structure of the amorphous state of matter and its relation to the liquid state. It is well known, even from the early observations of Friedrich¹ on the scattering of X-rays by wax and other amorphous solids and by Jauncey² on the scattering by glass, that the diffraction pattern in the case of glasses consists of diffuse haloes as in the case of liquids. This indicates that the arrangement of the molecules or atoms in the glassy state presents a closer analogy to that in the liquid than that in the crystalline state. Later, many inorganic glasses such as vitreous silica, borax glass, etc., have been investigated by workers in the field, notably Randall, Rooksby and Cooper, Zacharaisen, Wyckoff, Warren and others,³ with similar results.

This similarity in the X-ray patterns of the liquid and glass supports the fundamental conception that glass, though it possesses some of the mechanical properties of the solid state, is, nevertheless, to be regarded as an undercooled liquid characterized by optical isotropy and by lack of symmetry or periodicity in the macroscopic arrangement of the structural elements. The transition from the glassy to the liquid state does not take place at a precisely defined temperature and does not involve latent heat effects or any sudden change in the volume as in the case of the transition from the crystalline to the liquid state. Now, it is obvious that the real relation between the liquid and glassy states can only be understood by a detailed study of the changes which take place when an amorphous solid changes to a liquid and *vice versa*. The first attempt to approach the problem from this point of view is that of Dr Krishnamurthi⁴ in his X-ray study of some amorphous solids at the transition temperatures. He has followed up the changes in the diffraction haloes obtained in the case of ordinary rosin, shellac, and of a synthetic resin during the transition from the solid to the liquid state. He noticed that the sharp haloes obtained in the case of the solid became more

diffuse when the substance was melted. Besides, the transition was followed by a contraction in the diameter of the halo in the pattern and an increased scattering at small angles to the primary beam. These observations have been explained by him by means of the theory put forth by Raman and Ramanathan for X-ray diffraction in liquids and amorphous solids. In the light of these facts, some observations of the X-ray diffraction haloes given by liquids which are supercooled and made to pass into the vitreous condition would be of interest in order to further elucidate the nature of the glassy condition and particularly, to determine whether, when the temperature is taken below the softening point, any further rearrangement of molecules takes place. The present work is, hence, an attempt to study simultaneously some organic glasses and their corresponding liquids.

Experimental Technique

Viscous organic liquids when freed from dust and cooled down to low temperatures are known in many cases to assume the glassy state. In the present investigation, three substances which behave in this manner, namely glycerine, phenyl salicylate and benzophenone have been studied both in the glassy and liquid conditions. The samples were Kahlbaum's purest. Glycerine, which is a liquid at ordinary laboratory temperature, increases in viscosity as it is cooled down and begins to solidify at about 221°K , the temperature T_g at which it becomes a hard glass being 187°K . Phenyl salicylate (Salol) is a solid with the melting point 318°K . If melted and kept undisturbed, it remains a liquid at laboratory temperature 298°K . In order to avoid easy crystallisation, it was found necessary to distil the substance in vacuum. When the pure liquid is cooled, it sets itself as a glass at 238°K . Benzophenone (melting point 322°K) becomes glassy at 219.5°K . Many attempts to keep the two latter substances in the glassy state were unsuccessful, since slight variations of temperature of the glass brought about sudden crystallisation.

For photographing the X-ray diffraction patterns an ordinary flat film camera was used. The experimental arrangement employed in the present investigation was the same as in the powder photograph method of Debye and Scherrer. However, the arrangement had to be modified so that the specimen could be cooled to sufficiently low temperatures. The camera used for the purpose consisted of an air-tight rectangular box (shown in the figure) made of brass and lined inside with lead. The low temperature specimen holder was a copper rod 1.5 cm in diameter and 10 cm long, projecting up to about 4 cm inside the camera through a hole at the bottom fitted with a soft rubber stopper. The liquid was contained in a thin capillary

tube of lead-free glass which by itself did not give any observable diffraction pattern even with very long exposures to X-rays. The capillary tube with the liquid was inserted into a narrow hole which runs down axially to 2 cm from the end of the copper rod inside the camera. The X-ray beam, collimated by a long fine hole (diameter 6 mm) in a lead block, was allowed to traverse the specimen through a small transverse aperture (diameter 3 mm) which was opened out a little on the film side of the rod, so that the diffracted beam would not strike its edges. The specimen was cooled by keeping the whole length of the copper rod, projecting below the camera, dipped in liquid air. To minimise the effects of conduction from the surrounding air, the part of the rod inside the camera was covered by a thick layer of asbestos, leaving a clear path for the X-ray beam to traverse the specimen.

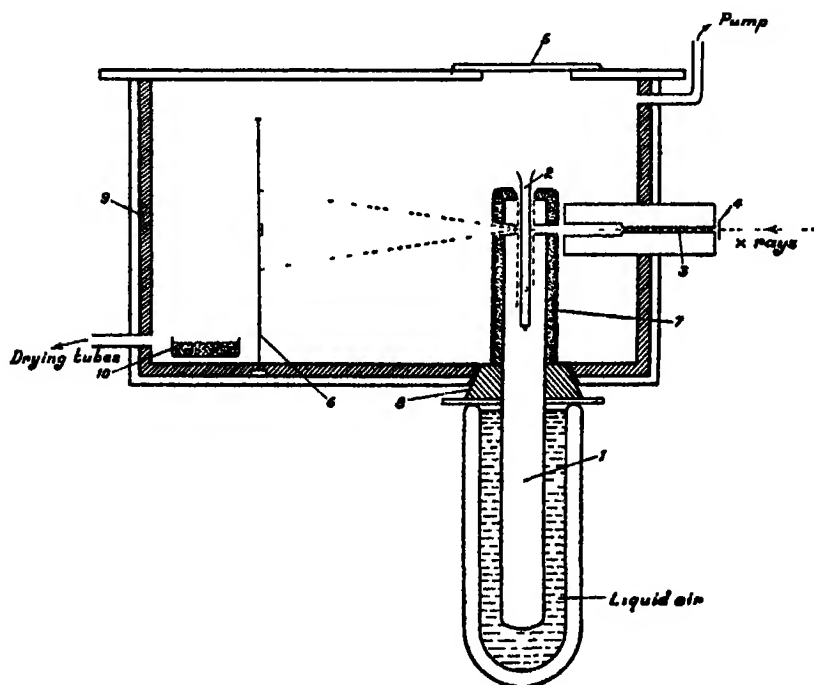


FIG 1 Schematic Diagram of the X-Ray Camera

- 1—Copper Rod, 2—Glass Capillary and the Specimen, 3—Slit, 4—Nickel Foil,
5—Glass Window, 6—Photographic Film, 7—Asbestos Covering,
8—Rubber Stopper, 9—Lead Lining, 10— P_2O_5

An easy method of avoiding the deposition of ice on the copper rod and the specimen when they were cooled down was to keep the air inside the camera perfectly dry. Hence the camera was covered up with another metal

plate, the joint between the cover plate and the camera was made air-tight with a putty supplied by Metropolitan Vickers. The camera was evacuated and dry air let in. To remove the water vapour which might still remain in the air, some flat dishes containing phosphorous pentoxide were previously placed inside the camera. The opening of the slit of the camera was closed by a nickel foil (thickness 0.6 mm). This foil, besides making the camera air-tight, also served as the filter for the X-radiation from the copper anti-cathode of the X-ray tube. It was certain that with this arrangement, the copper rod and consequently the specimen attained a temperature sufficiently low, since, on looking through a glass window at the top of the camera, the tendency for the formation of CO_2 flakes on the copper rod was quite visible.

The source of X-rays was a metal Shearer tube, excited by a transformer, the voltage applied being in the neighbourhood of 35 K V. The nickel filter used completely cuts off the $K\beta$ of copper, and the $K\alpha$ with $\lambda = 1.54 \text{ \AA}$ (though mixed with a little general radiation) that is transmitted, serves as the monochromatic X-ray beam. The photographic film was kept at a distance of 4.6 cm from the specimen. With a current of 6 milliamperes in the tube, exposures of the order of 8 hours were found necessary to obtain good diffraction patterns.

Results and Discussion

The results obtained in the case of all the substances are striking. A comparison of the negatives of the diffraction patterns for the liquid and the glass reveals in the latter (1) a considerable decrease in the scattering at small angles, (2) a conspicuous sharpening of the liquid haloes, and (3) a widening of the liquid haloes. Due to the complicated structure of the molecules, quantitative calculation by the method of Fourier analyses developed by Zernike and Prins⁶ was found to be very difficult and hence the results are recorded and explained in terms of the existence of Bragg reflection planes in the liquid. Results obtained from measurements of the negatives are recorded in Tables I, II and III. Column 2 in the tables gives the scattering angle for the direction of the maximum intensity in the halo. The spacings, calculated from the Bragg formula $d = \frac{\lambda}{2 \sin \theta/2}$ where θ is the angle between the direct and the diffracted beams, are given in Column 3. Columns 4 and 5 give the spacings calculated similarly, corresponding to the inner and outer limits to which the halo extends. The last column gives the difference of Columns 4 and 5, and serves to indicate the sharpness of the halo. The photographs are reproduced in Plate II. The observed effects are much more clear in the original negatives than in the prints.

TABLE I

Glycerine $C_3H_8O_3$ $T_g = 187^\circ K$

	θ	$d = \frac{\lambda}{2 \sin \theta/2}$ A U	Spacing of the inner limit A U	Spacing of the outer limit A U	Difference in the limits of spacing A U
Liquid . .	$19^\circ 34'$	4.49	4.91	3.96	95
Glass . .	$21^\circ 23'$	4.14	4.49	3.86	63

TABLE II

Phenyl Salicylate $C_{13}H_{10}O_3$ $T_g = 238^\circ K$

	θ	$d = \frac{\lambda}{2 \sin \theta/2}$ A U	Spacing of the inner limit A U	Spacing of the outer limit A U	Difference in the limits of spacing A U
Liquid {	1st halo .. $9^\circ 16'$	9.53			
	2nd ,, $17^\circ 30'$	5.06	5.71	4.63	1.08
	3rd ,,	.	4.63	2.59	2.04
Glass {	1st halo $10^\circ 10'$	8.69		.	
	2nd ,, .. $18^\circ 4'$	4.95	5.31	4.56	75
	3rd ,, .. $24^\circ 25'$	3.64	4.05	2.61	1.44

TABLE III

Benzophenone $C_{13}H_{10}O$ $T_g = 219^\circ 5 K$

	θ	$d = \frac{\lambda}{2 \sin \theta/2}$ A U	Spacing of the inner limit A U	Spacing of the outer limit A U	Difference in the limits of spacing A U
Liquid	$18^\circ 54'$	4.69	5.23	4.21	1.02
Glass	$20^\circ 0'$	4.43	4.9	4.16	74

In the case of liquid glycerine, earlier workers have got one prominent halo with comparatively little scattering at small angles. When the liquid solidifies, this main halo increases in diameter which shows a decrease in the spacing to the extent of 35 \AA . From Column 6 it can be seen that this halo is sharper than that of the liquid. The diffraction pattern for glycerine in the glassy state shows clearly the extent of the decrease in the scattering at small angles.

Liquid salol does not seem to have been investigated by X-rays till now. The liquid pattern consists of three more or less diffuse haloes, the innermost being very faint. The second one is very intense, and the third so faint and diffuse that it is not separated from the second. In the pattern for salol in the glassy state, all the haloes widen out and get so much sharpened that the second and third are well resolved and show themselves up as two separate haloes. Benzophenone gives a pattern similar to that of glycerine, the pattern for the glass showing markedly the widening and sharpening effects.

The above facts can be explained qualitatively by means of our conception of the physical changes taking place when the liquid solidifies to form the glass.

Scattering at Small Angles—In the particular case where the angle at which X-rays are scattered is very small, the ordinary classical theory of scattering of visible light, developed by Einstein and Smoluchowski for liquids, can be applied with sufficient justification, as was shown by Raman and Ramanathan⁷ in their theoretical consideration of the X-ray diffraction in liquids. Now, according to this classical theory of light scattering, the intensity of light scattered due to unit volume of a liquid is proportional to

$$\left(\frac{\mu^2 + 2}{3} \right) \frac{n^2 RT \beta}{N}$$

where μ is the refractive index of the liquid, n the total number of molecules in the liquid per unit volume, R and N the gas and Avogadro's constants respectively for gm. molecules, and β the isothermal compressibility of the liquid. In the above expression for intensity, both T and β decrease when the substance is cooled down and hence the intensity of scattered light at such small angles should decrease. When the liquid changes into glass, the decrease in compressibility is enormous, β for the hard glass being many times smaller than that for the liquid. Hence the large amount of decrease in the scattering of X-rays that is observed in the case of glasses, is quite consistent with the above considerations.

Sharpening of the Haloes—The sharpening of the liquid haloes in the glassy state can be considered to be due to the decrease in the fluctuation

of the mean molecular distance in the liquid. On account of the high viscosity of the glass, the molecules get almost fixed up in space and hence, the deviations of the molecular distances from the mean are considerably lessened. The ideal case where there is absolutely no fluctuation in the spacing will be the crystalline state where the diffraction pattern consists of very sharp rings. However, the case of glass is nowhere near that of the crystal, as is evident from the diffuseness of its haloes compared to the sharpness of the rings in the crystal pattern.

Widening of the Haloes—This is obviously due to a decrease in the mean molecular distance, for, according to the Bragg formula

$$\lambda = 2d \sin \theta/2$$

if d decreases, θ the angle at which the maximum scattering occurs increases. This decrease in the value of d in the case of the glass is a consequence of the nearing up of the molecules to form a closer packing in the solid condition.

Now, it is interesting to note that the above results are found to agree with those predicted by Raman and Ramanathan in their consideration of the influence of temperature on the liquid haloes. Their conclusions have been verified in the case of high temperatures by Ramasubramanian⁸ and Vaidyanathan.

Thus the above results indicate that when the temperature of the substance is lowered below the softening point, no radical rearrangement of the molecules other than those naturally due to the lowered temperature of the fluid takes place. This idea is supported by observations on light scattering in amorphous solids and undercooled liquids. Experiments on light scattering by glassy salol have shown that the light scattering power in the glassy and liquid states remains of the same order of quantities. Hence the constitution of glass can be considered to be fundamentally the same as that of the liquid, with the difference that in glass, the molecules are nearer each other than those in liquids with almost fixed positions for them, while in the case of liquid their positions are constantly varying.

In conclusion, the author takes this opportunity to record his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., under whose inspiring guidance the present investigation was carried out.

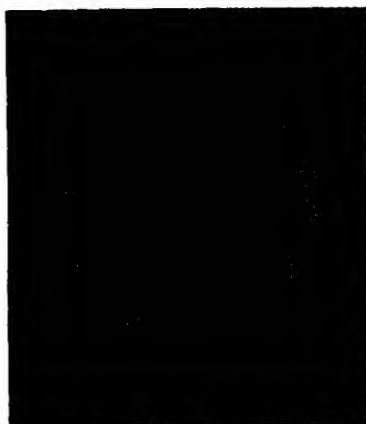
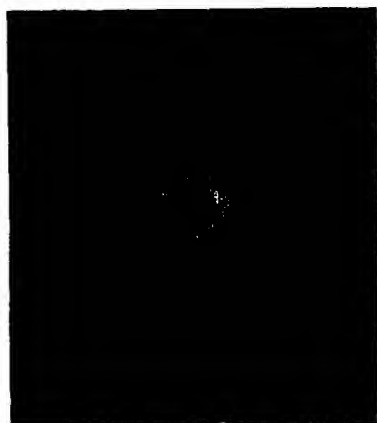
Summary

Using a modified form of the ordinary X-ray diffraction arrangements, three organic substances, namely glycerine, salol and benzophenone have

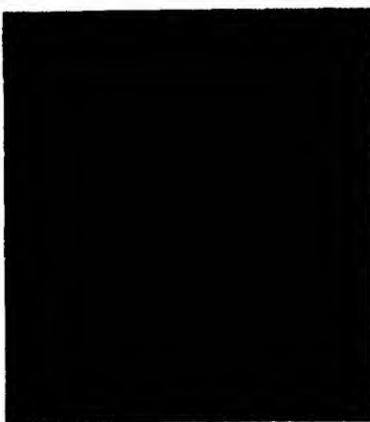
been investigated both in the liquid and glassy conditions by means of X-rays. The changes observed in the diffraction patterns when the liquid changes into glass are (1) a large decrease in the scattering at small angles with the primary beam, (2) a considerable sharpening of the haloes, and (3) a widening of the haloes. The first two effects have been explained by taking into consideration the large decrease in the compressibility of the substance as it changes from the liquid to the glassy state and the last one as due to the decrease of the intermolecular distance to form a closer packing of the molecules in the solid condition.

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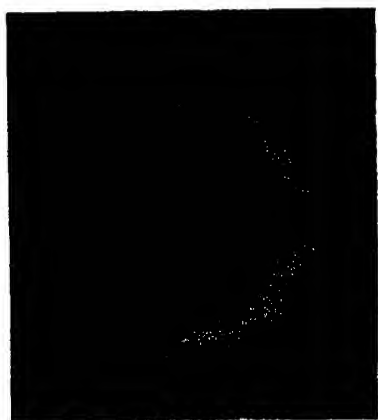
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Glycerine



Silol



Benzophenone

Liquid State

Glassy State

RAMAN SPECTRA OF SOME ORGANIC BI-CYCLIC COMPOUNDS.

Naphthalene, Decaline, Tetralin, Indene, *Trans*- β -Decalone, *Trans*- β -Decalol.

BY BISHAMBHAR DAYAL, SAKSENA

Received July 22, 1938

(Communicated by Sir C V Raman, Kt, FRS, N L)

1 Introduction

A knowledge of the complete spectra of molecules along with their polarisation character is of great importance in the elucidation of their molecular structure. The theory of groups is of great help in this direction. On this theory it is possible to calculate the number and nature of modes of vibration and their selection rules for any molecule possessing some elements of symmetry. According to Wigner¹ the number of oscillations a_p of the type of vibration p , is given by $a_p = \frac{1}{h} \sum \chi^{(p)} \epsilon(R)$

where $\epsilon(R) = \sum_{\text{rotation pure}} (u_R - 2) (1 + 2 \cos \phi) + \sum_{\text{rotation and reflection}} u_R (2 \cos \phi - 1)$

h is the number of elements of symmetry for a particular group, ϕ the angle of rotation for any particular element of symmetry (axis or plane) which does not alter the character of the group after rotation, u_R the number of points in any symmetry, and $\chi^{(p)}$ is the character of the irreducible representation of various types of elements of the group. Tables for the representation of such characters have been given by Tisza.² The number of polarised and depolarised lines for a given molecular structure can thus be found out and compared with the experimental data. The present paper gives the results of an investigation on the Raman spectra and depolarisation measurements of decaline, tetralin, indene, *trans*- β -decalone, *trans*- β -decalol and naphthalene, and these have been discussed in relation to the molecular structure.

2 Experimental

All the substances examined were in the liquid state except *trans*- β -decalol which was a solid. These were purest Kahlbaum's chemicals excepting *trans*- β -decalone and *trans*- β -decalol which were lent to the author by Dr M. A. G. Rau. These were further purified and twice distilled in vacuum.

into a Wood's tube. Two pyrex arcs were used for illumination, and a Hilger Littrow glass spectrograph having a dispersion of 10 Å U per mm in the 4358 region was used for photographing the spectra. The plates were measured on a Hilger cross-slide micrometer in comparison with an iron arc spectrum. The accuracy of measurement is about 2 cm^{-1} for sharp and intense lines.

The depolarisation measurements were made on a Fuess glass spectrograph of high light gathering power. The light from a quartz arc placed at the side was focussed by a glass condenser on the Raman tube which was carefully aligned to the axis of the spectrograph. A quartz double-image prism placed between the slit of the spectrograph and the observation end of the tube separated the scattered radiation into two components, vertical and horizontal, which were focussed by a lens on the slit of the spectrograph. The plate was then run on a microphotometer and the densities of lines in the two components were found out. In cases where the plate showed the background, the density of the line was obtained by subtracting the density of the background from the total density of the line. A set of intensity marks were obtained on the same photographic plate by the method of varying slit widths, using as a source of illumination, a small tungsten filament lamp fed by a current from a freshly charged battery at a constant voltage. Blackening— $\log I$ (intensity) curves were drawn for four wave-lengths by running this plate on the microphotometer. All the curves were parallel in their straight portions. The same curves were used for all the plates which were developed in the same strength of the developer for the same time. From the curve corresponding to $\lambda = 4358$, the intensities of the lines in the two components were read off from the known values of their densities and their depolarisation ratios obtained. The ratio determined in this way involves errors due to the spectrograph and other accessories. These were found by taking the spectrum of the direct unpolarised light from the mercury arc after it had passed through a double-image prism, and finding the ratio of intensities in the vertical and horizontal components in the manner stated above. This gave a value of 0.68 for the spectrographic correction. Without altering the experimental arrangements the depolarisation ratios for carbon tetrachloride lines were found and compared with the known values of depolarisation for these lines. Good agreement was observed on making the above correction.

3 Results

The results of investigation are tabulated in Tables I–VI. The following notation has been used for the assignment of lines :—

$\lambda = 4358 \ 34 \ e$	$\lambda = 4108 \ h$	$\lambda = 3663 \ o$
$= 1347 \ 50 \ f$	$= 4077 \ 8 \ i$	$= 3665 \ p$
$= 4339 \ 24 \ g$	$4046 \ 5 \ k$	$= 3650 \ q$
		$= 3906 \ m$
		$= 3984 \ l$

1 *Decaline*—The substance has been investigated previously by Bomino and Cella,³ Mukerji,⁴ Jatkar,⁵ Mitia,⁶ Mutsumo and Han.⁷ The following new lines have been observed in the present investigation 740, 970, 1079, 1124, 1451. The lines at 740 and 1144 appear as companions to the intense lines 752 and 1162. The agreement between the results of the previous workers and the author is fairly close. Of the lines recorded 18 are polarised and 19 depolarised.

2 *Tetralin*—The substance has been investigated by Bomino and Cella,³ Mukerji,⁴ Venkateswaran⁸ and Mutsumo and Han.⁷ The following new lines have been observed 788, 1088, 1273, 1293, 1329, 1393, 3036 and 3056. The lines at 1285 and 3049 reported by previous workers are split up into doublets at 1273 and 1293, and 3036 and 3056. The latter may be a combinational frequency given by $3036 = 1601 + 1532$, several doublets are present in the spectra and all the C—H frequencies between 2800 and 3100 excited by $\lambda = 4046$ are resolved into sharp lines, whereas in decaline they appear as broad lines. The wing accompanying the Rayleigh line in tetralin is stronger than in decaline. There are 21 depolarised and 20 polarised lines. The continuous spectrum in tetralin is depolarised.

3 *Indene*—This has been investigated by Hayashi,⁹ Manzoni-Ansidei,¹⁰ and Mutsumo and Han.⁷ The author's results agree very closely with those given by Ansidei, but Hayashi's values in general appear to be systematically lower. New frequencies have been observed at 2785, 987, 470 and 320. A great majority of lines show a value of ρ in the neighbourhood of .50.

4 *Trans- β -Decalone*—No previous investigation appears to have been made on this compound. It is a substitution product of decaline, two of the H atoms of which are replaced by an O atom in the β -position. The spectrum strongly resembles that of decaline, and has yielded 39 lines of which 22 are polarised and 15 depolarised.

5 *Trans- β -Decalol*—The substance was examined in the solid state by the method of complementary filters.¹¹ In spite of the fact that the substance was purified by repeated crystallisation, it was not possible to get rid of fluorescence. Hence the spectrum is not complete, only 8 lines being observed.

6 *Naphthalene*—Kahlbaum's pure naphthalene for analysis was distilled in vacuum and sealed in a double walled tube. The outer jacket was filled with water to ensure uniform heating and also to control temperature. As there was only a feeble background, it was possible to determine the depolarisation ratios of Raman lines. The spectrum of naphthalene has been examined by a number of workers—Petrikaln,¹² Kohlrausch and Dadien¹³ (solution), Zimecki¹⁴ (molten), Gockel¹⁵ (molten), Mutsuno and Han¹⁶ (solution), Manzoni¹⁷ (solution), Ananthakrishnan¹⁸ (solid), Canals and P. Pevrot¹⁹ (solid) and Kohlrausch.²⁰ According to the X-ray evidence,²¹ naphthalene possesses a centre of symmetry, and so the vibration spectrum should show only 24 lines. Only 10 lines have been reported for the molten state, 11 for solution, 16 lines for crystal. Pevrot and Canals report 24 lines for the crystal but the assignments are not all correct. One of the lines 702ff is in fact 1511 and is no new line. In the present case an intense picture was obtained under prolonged exposure and 21 lines were identified. The spectra reported by various workers are given below for comparison.

It may be seen from the table that the lines at 1168 and 1623 appear only in the solid. The line at 1280 in solid is shifted to 1250 in liquid, and two new lines at 191 and 397 are observed in the liquid. Otherwise the spectrum observed by the author contains all the lines reported by one or the other of previous workers.

Molten or solution						Crystal		
Kohlrausch and Dehen	Zimmerli	Goebel	Mutsumoto and Han	Mansoni	Author	Ananthakrishnan	Canals and Petrov	Kohlrausch
Solution	Fusion	Solution	Solution	Molten	Molten	Crystal	Crystal	Crystal
.	191 (1)	.	404 ff	.
..	.	512 (5)	514 (8)	510 (3)	397 (1)	511 (3)	518 Ff	513 (6)
505 (2)	511 (3)	.	.	.	511 (6)	.	702 ff	.
..	726 (1)	.	743 ff	728 (1)
.	742 (2)	761 (5)	764 (6)	760 (3)	760 (6)	764 (5)	764 F	766 (12)
762 (4)	762 (3)	778 (1)	.	.	772 (1)	.	.	786 (1)
.	941 (2)	.	.	.
836 (0)	1024 (5)	1019 (5)	1018 F	1023 (9)
1023 (2)	1026 (3)	1026 (4)	1028 (4)	1023 (3)	.	.	1108 ff	.
.	1142 (2)	1144 (8)	1144 ff	1148 (4)
1142 (0)	.	1153	.	1142 (1)	.	1168 (1)	.	1168 (2)
..	1206 (0)	.	1205 f	.
.	1239 (1)	1240 (2)	1243 f	1245 (2)
1245 (0)	.	1251 (0)	.	1239 (0)	1257 (2)	1280 (4)	1285 ff	1280 (2)
.	1326 (1)	1326 (0)	1322 F	1326 (4)
.	1323 (0)	1323 (1)	.	1320 (4)

Molten or solution						Crystal		
Kohlrausch and Dedieu	Zamecki	Goekel	Mutsumo and Han	Mauzoni	Author	Ananthakrishnan	Canals and Pevrot	Kohlrausch
Solution	Fusion	Solution	Solution	Molten	Molten	Crystal	Crvtal	Crystal
1377 (4)	1377 (0)	1379 (8)	1382 (8)	1377 (8)	1379 (15)	1379 (15)	1381 FF	1384 (20)
1412 (0)	1406 (0) *	.	.	.
.	1438 (2)	1440 (1)	1438 /F	1448 (2)
.	1460 (4)	1462 (4)	1464 (4)	1462 (3)	1460 (4)	1460 (5)	1462 F	1465 (8)
.	1530 (0)	.	.	.
1573 (3)	1575 (4)	1572 (3)	1577 (4)	1576 (3)	1576 (5)	1537 (7)	1576 F	1578 (8)
.	1623 (4)	1626 f	1628 (1)
.	2080 ff	.
.	3001 (1)	3007 ff	.
.	3025 (1)	3030 ff	.
3046 (1)	3058 (4)	3062 (4)	3046 (8)	3064 (8)	3058 (4)	3054 (12)	3058 F	3058 (4)
.	3244 (2)	.	3244 F	.

4 Discussion

For purposes of comparison the spectra of all compounds studied in the present paper are schematically represented in Fig 1. The frequency shifts of Raman lines are represented horizontally in wave numbers and the intensities are indicated by the heights of the lines. The figure by the side of each line indicates the value of the depolarisation ratio. Depolarised lines are crossed along their entire length. The letters δ (C - H), ν (C - H), C = O, C = C, C - C indicate the types of oscillations.

A general comparison of the spectra reveals the following facts —

(1) Certain Raman lines have fairly constant frequency shifts and depolarisation ratio in all the compounds. These are joined by dotted lines in the figure. They lie in the regions 400–500 cm^{-1} and 700–800 cm^{-1} . The ratio of the intensities of these lines as read from the microphotometer curves is 1.03 in naphthalene, 1.10 in decaline and 1.2 in tetralin. The intensity and depolarisation considerations lead us to conclude that these lines should be ring vibrations of the two fused rings.

(2) Besides the above lines there are two lines in all the compounds, one strong lying in the region 1019–1040, and the other of medium intensity, lying in the region 1075–1090 which change their polarisation characteristics as we pass from compounds containing the two benzene rings to compounds containing two cyclohexane rings. The first line appears polarised ($\rho = .43$) in indene, tetralin and naphthalene ($\rho = .55$), but is weak and depolarised in decaline and decalone. The other line is polarised in decaline and decalone and tetralin, but unpolarised in others. As benzene and its derivatives show a strong polarised line in the neighbourhood of 1000, while cyclohexane and its derivatives show a depolarised line near 1028, these lines may be expected to come out with the same intensity and polarisation in compounds containing the two fused benzene or cyclohexane rings.

(3) Raman lines having frequency shifts below 200 are present in all the compounds. They are very broad, fairly intense and completely depolarised in tetralin. Such broad low frequency lines are not generally observed in compounds possessing a single ring-like benzene and its derivatives. Therefore these lines may be attributed to the deformational oscillation of the two rings of these compounds against each other. It may be expected that in molecules possessing a puckered structure their oscillations would be more pronounced and the lines would come out with greater intensity. This may explain the greater intensity of these deformational oscillations in tetralin.

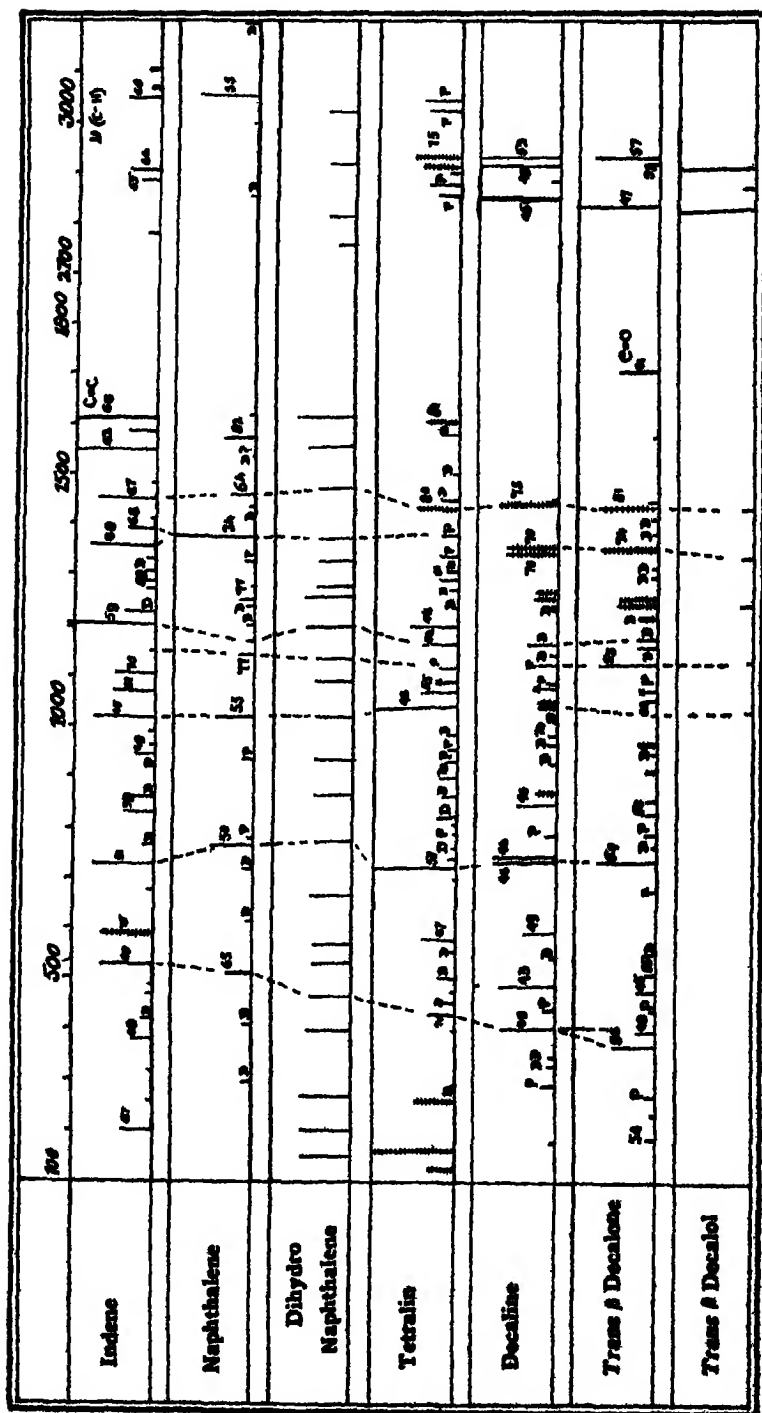
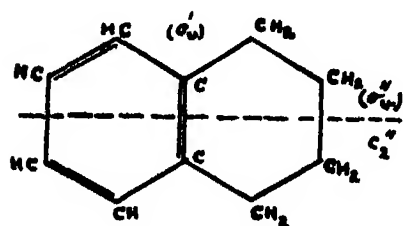


Fig 1

The infra-red spectra of decaline, tetralin and naphthalene have been investigated by Le Comte²² The spectra of decalin and naphthalene exhibit greater resemblance than that exhibited by the spectra of benzene and cyclohexane. The infra-red spectra given in Tables VII, VIII and IX show strong absorption bands at 740 and 939 cm^{-1} which are also exhibited by other compounds containing the naphthalene ring. These lines come out weakly in the Raman spectra

Tetralin—contains one benzene ring which is plane and one cyclohexane ring which is puckered. Dipole moment²³ measurements indicate a small electrical moment for the molecule. This may be either due to a puckered structure of the molecule or it may be due to a strain in the chemical bonds due to the fusion of the two rings. As the cyclohexane ring is puckered, the first is a likely possibility. Polarisation study of vibration lines in tetralin lends support to this view.



Tetralin

representations A_1, A_2, B_1, B_2 which are given below

If we regard all the carbon atoms in tetralin in one plane, the various elements of symmetry are (1) a binary axis C_2' , (2) a plane σ_v'' passing through this axis, (3) a plane σ_h which is the plane of the molecule and an identity E . The symmetry of the group is then C_{2v} , which admits of four irreducible re-

Type	Character table				Number of vibrations		Selection rules	
	E	C_2'	σ_h	σ_v''	Ring C_{10}	Molecule $C_{10}H_{12}$	Raman	Infra-red
A_1	1	1	1	1	9	19	pol	α
A_2	1	1	-1	-1	4	12	dep	α
B_1	1	-1	1	-1	8	18	dep	α
B_2	1	-1	-1	1	3	11	dep	α
ν_a	22	0	14	0	for molecule $C_{10}H_{12}$			
ν_b	60	2	14	0				

The calculation shows that 19 polarised and 41 depolarised lines are to be expected if all the carbon atoms lie in one plane—the plane of molecule σ_h . If, however, the molecule is puckered, the puckering can occur only in the cyclohexane ring, for the benzene ring is known to be plane. Further the

two carbon atoms directly linked to the benzene ring must lie in the plane of the ring, and the two other atoms can lie in the plane of other atoms or displaced from it. In the latter case there will be no axis of symmetry C_2'' but the plane σ_v'' can still exist if both atoms are displaced to one side of the plane σ_h . In this case the group symmetry becomes C_{2v} , the two elements of symmetry being E and σ_v'' .

Type	Character table		Number of vibrations		Selection rules	
	E	σ_v''	Ring	Molecule	Raman	Infra red
A_1	1	1	12	30	pol	α
A_2	1	- 1	12	30	dep	α
ν_R	22	0				
ϵ_R	60	0				

The calculation shows that 30 polarised and 30 depolarised lines are to be expected for the given puckered structure. In tetralin, 46 lines have been recorded, of these 20 are polarised and 21 depolarised. The polarisation measurements therefore appear to support the requirements of a puckered structure better than that of a plane.

The infra-red absorption maxima of tetralin are recorded in the following table

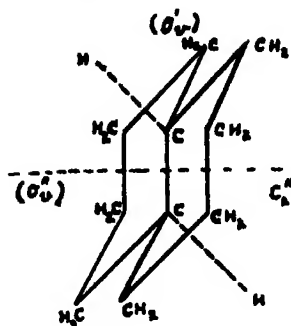
TABLE VII

Infra red	741 (α)		785 (α)	806 (α)		858	893
Raman	744 (0)		789 (0)	805 (0)	843	868 (0)	904 (0)
Infra red	939 (α)		975 (w)	1022 (w)		1053 (w)	
Raman	938 (0)		982 (0)		1037 (α)		
Infra-red		1100 (α)		1227	1266		1429 (α)
Raman	1088 (2)		1118 (2)	1234 (0)	1273 (3)		1432 (5)

The coincidence of infra-red and Raman lines shows definitely that the molecule has no centre of symmetry.

Decaline—exists in two isomeric forms as *cis* and *trans*-decaline. The polarisation characteristics of *cis* and *trans*-decalines can be easily calculated on the group theory.

(a) *Trans-form*—The elements of symmetry in this case are (1) a binary axis C_2'' , (2) a plane σ_v' perpendicular to the axis and the plane of

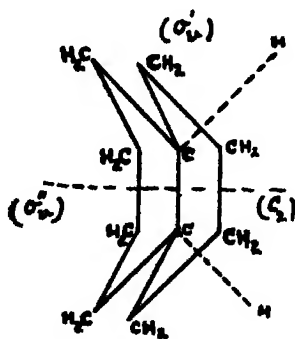
Decaline—*trans*

paper, (3) a centre of symmetry i and an identity E . The symmetry of the molecule is therefore C_{2h} . The number of vibrations and the character table is given below

Type	Character table				Number of vibrations		Selection rules	
	E	C_2	$\sigma_{v'}$	i	Ring C_{10}	Molecule $C_{10}H_{18}$	Raman	Infra-red
A_1	1	1	1	1	7	21	pol	α
A_2	1	1	-1	-1	6	19	f	a
B_1	1	-1	1	-1	6	20	f	a
B_2	1	-1	-1	1	5	18	dep	α
ν_R	28	0	4	0	} for molecule $C_{10}H_{18}$			
ϵ_R	78	2	4	0				

[f -forbidden, α -inactive, a -active]

(b) *Cis-form*—The elements of symmetry in this case are (1) a binary axis C_2 perpendicular to the plane of paper and (2) two planes $\sigma_{v'}$ and $\sigma_{v''}$

Decaline—*cis*.

passing through this axis and (3) an identity. The symmetry is therefore C_{2v} . The number of vibrations can therefore be written as follows :

Type	Character table				Number of vibrations		Selection rules	
	E	C_2	σ_v'	σ_v''	Ring C_{10}	Molecule $C_{10}H_{18}$	Raman	Infra red
A_1	1	1	1	1	7	21	pol	a
A_2	1	1	-1	-1	6	19	dep	na
B_1	1	-1	1	-1	6	20	dep	a
B_2	1	-1	-1	1	5	18	dep.	a
ν_R	28	0	4	0	} for molecule $C_{10}H_{18}$			
ϵ_R	78	2	4	0				

These calculations show that 21 polarised and 57 depolarised lines are to be expected in the spectrum of *cis*-decaline while 21 polarised and 18 depolarised lines are to be expected in the spectrum of *trans*-decaline.

To verify these numbers it is necessary to get *cis* and *trans* spectra separately. In the present investigation the decaline used is a mixture of *cis* and *trans* molecules, the *trans*-form predominating. The spectrum of decaline shows a number of pairs of fine lines, one in each pair can be assigned to the *cis*- and the other to the *trans*-form. The detection of such lines has been facilitated by the use of a high dispersion spectrograph. Such pairs are to be expected in the spectra of mixtures of *cis* and *trans* isomers, because, as the structures of the two forms are not very different, the frequency differences between the vibration lines of the two forms cannot be expected to be large. In order to assign the lines to the *cis*- and *trans*-forms, the following procedure was adopted. A comparison was first made with the spectrum of *trans*- β -decalone which is completely *trans*, and *trans* lines isolated. These are then compared with the infra-red spectrum of decaline as reported by Le Comte. The infra-red lines for the *trans*-form of decaline are forbidden in Raman effect, and therefore the infra-red lines which are present as Raman lines should belong to the *cis*-form of decaline. The infra-red spectrum of decaline is given in Table VIII.

It appears that the strong sharp line at 741 is the symmetric oscillation of the *cis*-form whereas 751 is the symmetric oscillation of the *trans*-form. Barring the lines 785, 835, 917, 1414, all the others may be taken as representative of the *cis*-form.

TABLE VIII

Infra-red	741 (s)	798 (w)	835 (w)		917 (w)		939 (s)
Raman	740 (3)	798 (1)					932 (0)
Infra-red	1022 (0)	1220 (w)		1200 (w)		1414 (w)	
Raman	1018 (0)	1233 (0)		1273 (2)			

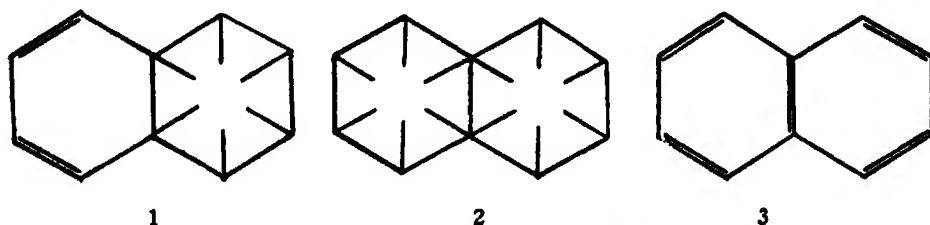
The following lines may thus be assigned to *cis*- and *trans*-forms

<i>Cis</i> form			<i>Trans</i> form		
Jatkar	Author		Jatkar	Author	
	$\Delta\nu$	ρ		$\Delta\nu$	ρ
	329 (0)	D		180 (0)	D
539 (0)				406 (5)	7
595 (3)	595 (3)	53		446 (1)	P
	740 (3)	46	491 (5)	491 (5)	45
794 (1)	798 (0)	D		547 (0)	D
	932 (0)	D		751 (3)	45
	1018 (1)	D		848 (4)	47
1040 (2)	1046 (2)	D	881 (3)	875 (2)	70
	1088 (1)	P	957 (1)	970 (0)	D
	1124 (2)	P	996 (2)	988 (1)	D
	1162 (2)	D		1056 (2)	D
	1134 (0)	D		1079 (2)	P
	1233 (0)	D	1145 (3)	1144 (1)	D
1270 (5)	1273 (2)	D	1234 (1)	1242 (0)	D
1347 (3)	1348 (6)	D		1254 (0)	D
			1363 (5)	1358 (5)	.8
				1444 (6)	.8

The results of the author agree with those of Jatkar,⁵ who worked with a concentrated form of *trans*-decaline. If we take the region 0 — 1200 as belonging to the carbon ring we find 5 polarised and 7 depolarised lines which show good agreement with the calculated number of 7 polarised and 5

depolarised lines. In the *cis*-form we find 8 polarised and 15 depolarised lines which agree with the calculated number of 7 polarised and 17 depolarised lines

Naphthalene—The molecule of naphthalene contains two fused benzene rings, but on account of the different chemical behaviour of the two rings, three different types of structural formulæ have been proposed for the



Structural formulæ of naphthalene molecule

1. Willstätter and Wäser. 2 Bamberger. 3 Erlenmeyer

molecule, viz, those of Erlenmeyer, Bamberger²⁴ and Willstätter and Wäser²⁵. The first two, marked 3 and 2, have a symmetry D_{2h} , the elements of symmetry being the three binary axes C_2'' , C_2' , and C_2 , the three planes of symmetry, σ_v'' , σ_v' , σ_h the last named being the plane of molecule, and a centre of symmetry i , and an identity. The following tables give the character table as well as the number of vibrations for symmetry D_{2h} . There are 8 modes of irreducible representation

Type	Character table								Number of vibrations		Selection rules	
	E	C_2	C_2^1	C_2''	i	σ_h	σ_v'	σ_v''	Ring C_{10}	Raman	Raman	Infra
A_1	1	1	1	1	1	1	1	1	5	9	pol	ω
A_2	1	1	-1	-1	1	1	-1	-1	4	8	dep	ω
B_1	1	-1	1	-1	1	-1	1	-1	1	3	dep	ω
B_2	1	-1	-1	1	1	-1	-1	1	2	4	dep.	ω
A_1'	1	1	1	1	-1	-1	-1	-1	2	4	f	f
A_2'	1	1	-1	-1	-1	-1	1	1	2	4	f	a
B_1'	1	-1	1	-1	-1	1	1	-1	4	8	f	a
B_2'	1	-1	-1	1	-1	1	-1	1	4	8	f	a
ω_R	18	0	2	0	0	18	2	0				
ϵ_R	48	2	0	2	0	18	2	0				

In the third case the symmetry is C_{2v} , the elements of symmetry being C_2 (binary axis), σ_v the plane passing through this axis, and σ_h the plane of the molecule. The number of vibrations is given in the following table

Type	Character table				Number of vibrations		Selection rules	
	E	C_2	σ_h	σ_v	Ring C_{10}	Molecule $C_{10}H_8$	Raman	Infra red
A_1	1	1	1	1	9	17	pol	a
A_2	1	1	-1	-1	4	8	dep	na
B_1	1	-1	1	-1	8	14	dep	a
B_2	1	-1	-1	1	3	9	dep	a
ν_R	18	0	18	0	} for molecule $C_{10}H_8$			
ϵ_R	48	2	18	0				

Kohlrausch²⁶ and Bonino²⁷ have also discussed the symmetry of the naphthalene molecule. According to the above calculation we should expect 9 polarised and 15 depolarised lines for the molecule for symmetry D_{2h} and 17 polarised and 31 depolarised lines for symmetry C_{2v} . In the present investigation 21 lines have been observed of which 9 are polarised and 12 depolarised. In the region 0—1200 belonging to the ring, we find 5 polarised and 5 depolarised lines, the number calculated for symmetry D_{2h} being 5 polarised and 7 depolarised lines. Further in the infra-red 17 lines out of 20 expected lines have been observed. All the above facts are fully in agreement with the symmetry D_{2h} of the naphthalene molecule. In this symmetry, the molecule has a centre of symmetry and, therefore, the frequencies corresponding to infra-red absorption are forbidden in Raman effect. Infra-red spectra of naphthalene have been investigated by Stang²⁸ and Le Comte²⁹. The infra-red and Raman lines and their polarisation characters are shown in Table IX.

It is clear from the table that the positions of infra-red and Raman lines do not coincide, which fact is in accordance with symmetry D_{2h} . The polarisation values of naphthalene lines such as 511, 764, 1024 are quite in agreement with the values found for these lines in other substances. The line 1379 is very strong and highly polarised and so appears to be a breathing frequency of the molecule.

TABLE IX

Raman	3244 D	3058 P							1578 D
Infra-red Raman	1530 D		3030 1460 P	1438 D	2380 1406 D	1940	1724 1378 P	1584 1326 P	
Infra red Raman	1230 D	1492	1205 D	1142 D		1389 1024 P			1275 941 P
Infra red Raman		1220		772 P	1125 760 P	728 D	1000	961	511 P
Infra-red Raman	881 397 D	820 191 D	782				714	623	

Indene—Indene contains one benzene and one pentadiene ring. The spectrum of indene closely resembles that of dihydronaphthalene. The molecule is very unsymmetric, and so nothing can be inferred from polarisation data.

Trans- β -decalone.—The spectrum of this substance agrees with that of decaline, but all the frequencies are in general lowered. However, there are some striking differences in the spectra of the two substances. The line at 375 which is weak and depolarised in decaline appears strong and polarised in decalone, and the strong line at 491 in decaline is replaced by two weak lines one polarised and another depolarised in decalone. The δ (C—H) vibration in decalone shows three shifts 1417, 1441, 1447 which agree with those observed in cyclohexanone in the same region. The C = O shift in decalone has the same shift and depolarisation as in cyclohexanone.

Finally the author desires to express his grateful thanks to Professor Sir C. V. Raman for his kind interest and helpful guidance. Thanks are also due to Dr. C. S. Venkateswaran for helpful discussion and to Dr. M. A. G. Rau for the loan of chemicals.

Summary

The Raman spectra of naphthalene, decaline, tetralin, indene, *trans- β -decalone* and *trans- β -decalol* have been studied, the last two for the first time. Polarisation measurements have also been made in the case of all these compounds excepting *trans- β -decalol*. The molecular structures of decaline, tetralin and naphthalene have been studied in the light of polarisation data and the symmetries of the molecules. The results indicate a puckered structure for tetralin, and a centro-symmetric structure for naphthalene. In decaline the *cis* and *trans* lines have been separated, the observed polarisation characteristics of these forms agree with the group theory results.

The determination of the values of ρ for all these substances has been made for the first time, and the results are given in Tables I-VI

TABLE I
Decaline

No	λ	$\bar{\nu}$	I	Assignment	No	λ	$\bar{\nu}$	I	Assignment
1	4998.126	20002	1	e-2936	25	4525.97	22089	5 s	e-849
2	4994.016	20018	2	e-2920	26	4514.90	22142	1 s	e-796 } f-849 }
3	4979.48	20083	2	e-2855	27	4505.85	22187	5 s	e-751
4	4651.19	21495 21503	6 b 0	e-1443 } e-1451 }	28	4503.83	22197	5 s	e-741
5	4638.02	21555	0	f-1443	29	4492.0	22255	1	e-683 } f-741 }
6	4632.73	21579	2 d	e-1359	30	4474.45	22347	5	e-595
7	4630.27	21591	3 d	e-1347	31	4464.10	22395	1	e-543 } f-595 }
8	4620.0	21639	0	f-1355	32	4457.69	22447	0	e-491
9	4612.45	21664	2 s	e-1274	33	4444.70	22492	1	e-446 } f-491 }
10	4610.49	21684	2 s	e-1254	34	4436.8	22532	6	e-406
11	4608.13	21695	0	e-1243	35	4430.85	22563	1	e-375
12	4605.59	21707	0	e-1231	36	4425.64	22589	1	e-349
13	4591.55	21773	10 d ⁵	e-1165 } k-2932 }	37	4416.0	22644	0	m-2948 } e-294 }
14	4587.44	21793	10 d	e-1145 } k-2912 }	38	4393.2	22757	0	e-180
15	4582.76	21815	2	e-1125 } k-2890 }	39	4387.6	22785	0	e-153
16	4575.48	21850	(1)	e-1088 } f-1145 }	40	4298.14	23259	6	k-1446
17	4573.71	21858	10 b	e-1080 } k-2847 }	41	4282.41	23345	3	k-1300
18	4568.66	21882	2 s	e-1056	42	4280.57	23355	1	k-1350
19	4566.80	21892	2 s	e-1046	43	4266.34	23433	2	k-1272
20	4567.11	21923	1 b	e-1015	44	4262.98	23451	2	k-1254
21	4553.89	21951	1	e-967	45	4260.95	23463	1	k-1242
22	4542.50	22008	0	e-930	46	4258.88	23473	1	k-1232
23	4533.81	22050	1	k-965	47	4245.93	23545	2	k-1160
24	4531.4	22062	1	e-876	48	4242.89	23562	1	k-1143
					49	4239.5	23581	0	k-1124

TABLE I—(Contd.).

No	λ	$\bar{\nu}$	I	Assignment	No	λ	$\bar{\nu}$	I	Assignment
50	4232.86	23618	0	$k-1087$	64	4146.64	24109	5	$k-596$
51	4231.24	23627	0	$k-1078$	65	4139.05	24154	0	$k-551$
52	4227.44	23648	4 s	$k-1057$	66	4128.80	24213	6	$k-492$
53	4225.59	23658	4 s	$k-1047$ $\tau-849$	67	4114.21	24299	6	$k-406$
54	4219.34	23694	1 d	$k-1011$	68	4109.80	24325	0	$k-375$
55	4215.28	23716	1 b	$k-989$	69	4104.10	24359	2 band	$k-346$ $o-2036$
56	4211.44	23738	1 b	$k-967$	70	4101.69	24374	2 band and line	$k-331$ $o-2920$
57	4206.9	23770	0	$k-935$	71	4092.86	24415	4 (b)	$k-290$ $p-2938$
58	4194.83	23832	1	$k-873$	72	4091.58	24433	4 bd	$q-2929$ $o-2855$
59	4190.49	23857	5	$k-848$	73	4087.93	24455	4 bd	$q-2936$
60	4181.70	23907	0	$k-798$ $\tau-595$	74	4085.30	24471	4 bd	$p-2968$ $q-2920$
61	4173.6	23953	5	$k-752$	75	4074.8	24534	4 bd	$q-2854$
62	4171.67	23965	3	$k-740$					
63	4162.20	24019	0	$k-686$ $\tau-491$					

$\Delta\bar{\nu}$	150 (0)	180 (0)	294 (0) ?	329 (0)	347 (0)	375 (1)	406 (5)
ρ	..	D	P	D	D	D	.69
$\Delta\bar{\nu}$	440 (1)	491 (5)	547 (0)	595 (3)	684 (0) ?	740 (3)	751 (3)
ρ	P	.43	D	.49	P ?	.46	.46
$\Delta\bar{\nu}$	798 (1)	848 (4)	875 (2)	930 (0)	970 (1)	988 (1)	1012 (0)
ρ	P	.46	D	D ?	D	.70	D
$\Delta\bar{\nu}$	1046 (2)	1056 (2)	1079 (1)	1088 (1)	1124 (2)	1144 (0)	1162 (2)
ρ	.75	.75 ?	P	P	P	D	D
$\Delta\bar{\nu}$	1234 (0)	1242 (0)	1254 (2)	1273 (2)	1348 (5)	1359 (5)	1444 (6)
ρ	D	D ?	.80	.80	.70	.70	.75
$\Delta\bar{\nu}$	1451 (0)	2655 (1)	2855 (8)	2890 (0)	2920 (8)	2936 (8)	
ρ	D	.	.45		.45	.52	

TABLE II.

Tetralin

No	λ	$\bar{\nu}$	I	Assignment	No	λ	$\bar{\nu}$	I	Assignment
1	5028.3	19882	1	e-3056	26	4578.22	21794	3	f-1201 } k-2919 }
2	5023.2	19902	1	e-3036	27	4581.52	21821	3 s	e-1117
3	5017.5	19925	1	e-3013	28	4577.55	21839	2	k-2866
4	4999.6	19996	2	e-2942	29	4575.99	21847	2 s	e-1091
5	4993.9	20019	1	e-2919	30	4571.81	21867	5	e-1071 } k-2838 }
6	4984.6	20033	0	e-2905	31	4564.82	21900	10	e-1038
7	4979.7	20076	1	e-2862	32	4556.13	21942	0	e-996
8	4972.8	20104	0	e-2834	33	4554.17	21952	1	e-986 } f-1038 }
9	4886.0	21374	6 s	e-1604	34	4543.31	22004	1	e-934 } g-1038 }
10	4680.6	21359	2 s	e-1579	35	4536.64	22036	0	e-902
11	4668.9	21393	1	f-1602	36	4529.62	22071	0	e-867
12	4663.3	21438	0	e-1500	37	4519.77	22119	1	e-819
13	4652.1	21489	1	e-1449	38	4517.26	22131	1	e-807
14	4648.6	21506	5	e-1432 } i-3010 }	39	4513.95	22147	0	e-789
15	4640.5	21543	0	e-1395	40	4508.08	22176	0	e-762
16	4636.8	21560	2	e-1378 } f-1435 }	41	4504.12	22196	0	e-742
17	4630.99	21596	2	e-1342 } i-2919 }	42	4500.63	22213	10 s	e-725
18	4628.36	21610	1 s	e-1328	43	4496.02	22236	0	e-702
19	4622.32	21628	2 s	e-1310	44	4489.64	22267	1	f-725
20	4618.50	21646	4 s	e-1292 } k-3057 }	45	4483.00	22300	0	g-725
21	4614.31	21666	2 s	e-1272 } k-3034 }	46	4471.57	22357	5	e-581
22	4606.22	21694	0	e-1248	47	4465.72	22386	0	e-552
23	4606.65	21702	0	e-1236	48	4456.14	22435	2	e-503
24	4599.06	21737	6	e-1201	49	4446.32	22484	1	e-454
25	4592.65	21768	5	e-1170 } k-2937 }	50	4441.85	22507	4	e-431
					51	4432.0	22537	00	m-3036

TABLE II—(Contd.)

No	λ	$\bar{\nu}$	I	Assignment	No	λ	$\bar{\nu}$	I	Assignment
52	4435.5	22547	00	m-3056	80	4218.95	23700	0	k-1005
53	4414.52	22646	0	e-292 m-2046	81	4214.52	23721	0	k-984
54	4408.76	22676	5	e-262	82	4205.50	23772	0	k-934
55	4389.00	22778	8	e-160	83	4201.81	23792	0	k-913
56	4382.74	22816	3	e-122	84	4191.06	23842	1	k-863
57	4367.58	22882	3	g-157	85	4184.89	23889	1	k-826
58	4352.74	23096	2	e-158	86	4182.76	23901	0	k-804
59	4327.52	23101	8	k-1604	87	4180.01	23917	0	k-788
60	4323.15	23125	3	k-1580	88	4175.42	23943	0	k-762
61	4308.86	23201	1	k-1504	89	4171.59	23965	0	k-742
62	4307.20	23210	0	v-1307	90	4168.62	23982	10	k-725
63	4300.9	23244	0	v-1272	91	4164.42	24006	1	k-701
64	4296.37	23258	1	k-1447	92	4143.43	24127	4	k-580
65	4295.58	23273	5	k-1432	93	4140.18	24147	0	k-554
66	4287.97	23314	0	k-1391	94	4130.56	24203	2	k-502
67	4285.82	23326	1	k-1379	95	4128.77	24213	0	k-492
68	4281.16	23358	1	k-1347	96	4126.30	24228	0	k-477
69	4278.10	23375	2	k-1330 e-437	97	4122.97	24247	3	k-458
70	4270.22	23411	1	k-1294	98	4118.38	24276	3	k-429
71	4266.67	23431	0	k-1274	99	4115.06	24296	0	k-409 p-3057
72	4260.48	23469	0	k-1236	100	4111.99	24312	2	k-393
73	4257.80	23480	0	v-1036	101	4108.12	24335	2	p-3018 q-3053
74	4253.29	23504	6	k-1201	102	4106.15	24347	2	v-162 q-3041
75	4245.73	23546	(1)	k-1159	103	4103.87	24367	2	o-2919
76	4237.35	23593	0	k-1112	104	4095.08	24413	3	k-292 p-2960
77	4232.0	23619	0	k-1086	105	4089.1	24448	4	k-237 p-2905
78	4229.19	23639	1	k-1066					
79	4223.95	23668	10	k-1037 e-780					

TABLE II—(Contd)

No	λ	$\bar{\nu}$	I	Assignment	No	λ	$\bar{\nu}$	I	Assignment
106	4086.56	24463	1	o-2830 } q-2919 }	108	4066.5	24594	2	k-121
107	4070.5	24547	3		109	4026.1	24831	0	k-121
$\overline{\Delta\nu}$	121 (3)	160 (8)	260 (5)	430 (4)	456 (1)	503 (2)	553 (0)	580 (4)	
ρ	D	.80	.74	.70	D	P	P	67	
$\overline{\Delta\nu}$	701 (0)	725 (10)	742 (0)	762 (0)	789 (0)	805 (0)	819 (2)	865 (1)	
ρ	P	.51	D	P	P	D ?	D	D	
$\overline{\Delta\nu}$	902 (2)	934 (1)	988 (1)	1037 (10)	1068 (2)	1088 (1)	1117 (1)		
ρ	P	P	D	46	D	P ?	P		
$\overline{\Delta\nu}$	1165 (2)	1201 (6)	1236 (0)	1273 (1)	1293 (2)	1310 (1)	1328 (1)		
ρ	D	.48	D	D	.61		P		
$\overline{\Delta\nu}$	1342 (2)	1381 (2)	1393 (0)	1432 (5)	1448 (2)	1502 (0)	1579 (2)		
ρ	P	P	..	.80	D	D	D		
$\overline{\Delta\nu}$	1604 (4)	2836 (3)	2862 (3)	2905 (2)	2919 (4)	2942 (6)			
ρ	.81	P	P		D	.71			
$\overline{\Delta\nu}$	3013 (1)	3036 (4)	3056 (4)						
ρ		P	P						

TABLE III
Indene

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
1	5043.0	19824	0	e-3114	26	4547.1	21973	1	e-965 } f-1022 }
2	5032.2	19863	1	e-3075	27	4545.54	21993	3 s	e-945
3	5028.0	19883	1	e-3055	28	4541.04	22016	1	e-922
4	4993.6	20028	(0)	e-2910	29	4528.61	22076	2 s	e-862
5	4988.6	20048	1	e-2890	30	4522.11	22107	3 s	e-831
6	4960.6	20153	0	e-2785	31	4514.07	22147	0	f-860
7	4687.3	21328	10 s	e-1610	32	4508.76	22173	1	e-765 } f-831 }
8	4682.9	21348	3 s	e-1590	33	4501.66	22208	6 s	e-730
9	4674.8	21385	10 br	e-1553 } f-1610 }	34	4512.6	22263	1	e-675 } f-732 }
10	4662.6	21442	3	e-1496 } f-1553 }	35	4473.61	22347	5	e-591
11	4654.02	21482	6	e-1456	36	4461.96	22405	5 s	e-533 } f-590 }
12	4640.7	21542	3	e-1396 } f-1453 }	37	4454.4	22443	0	e-490
13	4633.2	21577	6 s	e-1361	38	4449.9	22465	(1)	f-533 } e-473 }
14	4628.97	21602	1	e-1336	39	4440.0	22516	1	e-422
15	4622.03	21630	4 db	f-1365 } e-1308 } k-3075 }	40	4431.85	22557	2	e-381
16	4618.1	21648	3 br	e-1290 } k-3057 }	41	4420.0	22618	1	e-320
17	4615.39	21661	4 bd	e-1277 } k-3044 }	42	4408.3	22678	0	m-2914
18	4604.8	21710	3 s	e-1227	43	4397.2	22735	3	e-203
19	4600.22	21732	6	e-1206	44	4388.57	22790	0	f-205
20	4587.67	21790	1	e-1148 } f-1206 }	45	4328.35	23097	6	k-1606
21	4582.47	21816	2	k-2890	46	4324.82	23116	2	k-1589
22	4579.96	21831	4 d	e-1107	47	4317.72	23154	6	k-1551
23	4571.94	21866	4 s	e-1072	48	4307.0	23211	0	k-1494
24	4561.33	21917	6 s	e-1021	49	4300.19	23248	4	k-1457
25	4554.80	21950	(00)	e-988	50	4288.28	23313	4	k-1392
					51	4282.4	23345	4	k-1360

TABLE III—(Contd.)

No	λ	$\bar{\nu}$	I	Assignment	No	λ	$\bar{\nu}$	I	Assignment
52	4272.5	23398	1	k-1307	67	4175.67	23942	0	k-763
53	4269.0	23418	(0)	k-1287	68	4173.60	23953	0	k-752
54	4267.0	23429	1	k-1276	69	4169.66	23976	6	k-729
55	4257.68	23480	2	k-1225	70	4145.87	24114	3	k-591
56	4253.80	23502	6 v	k-1203	71	4141.0	24142	(0)	e-1204
57	4245.0	23555	0	k-1150	72	4135.54	24174	3	k-531 } o-3075)
58	4237.63	23599	3	k-1100*	73	4128.0	24218	1	k-487
59	4229.41	23637	(2)	k-1068*	74	4125.64	24243	1	k-467
60	4220.62	23687	(4)	k-1018	75	4117.57	24279	2	k-426 } p-3075)
61	4215.2	23718	(0)	k-987	76	4110.44	24322	2 d	k-383 } p-3037)
62	4211.5	23738	(0)	k-967	77	4100.7	24379	2 d	k-326
63	4207.6	23760	(2) d	k-945	78	4095.98	24407	2 d	o-2885
64	4203.0	23786	2 d	k-919	79	4090.41	24441	2 band	k-264 } q-2940 ?)
65	4192.58	23845	1	k-860					
66	4187.56	23874	3	k-831*					

* Shows a doublet structure in the lines

$\Delta\nu$	203 (3)	320 (0)	381 (2)	422 (1)	470 (0)	489 (0)	532 (5)
ρ	.67	..	.69	P	.		.69
$\Delta\nu$	591 (5)	675 (0)	729 (6)	764 (1)	831 (3)	861 (2)	931 (1)
ρ	.75		.51	D	.59	D	P
$\Delta\nu$	945 (2)	965 (0)	987 (0)	1019 (8)	1070 (4)	1106 (4)	
ρ	.69			.45	.61	70	
$\Delta\nu$	1204 (8)	1227 (3)	1276 (2)	1288 (1)	1307 (1)	1336 (1)	
ρ	.59	D	.59	P	D	D	
$\Delta\nu$	1360 (6)	1394 (3)	1456 (6)	1495 (0)	1552 (8)	1589 (2)	
ρ	.68	D	.68	.	.62	D	
$\Delta\nu$	1609 (8)	2785 (1)	2890 (2)	2910 (3)	3055 (3)	3075 (1)	3114 (1)
ρ	.68		.65	.66	.60	.	..

TABLE IV.
Trans- β -Decalone

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
1	4998.5	19990	6 br	e-2948	29	4492.10	22255	1	f-739 } e-683 }
2	4994.29	20011	2	e-2027	30	4486.0	22385	1	e-553
3	4974.84	20095	6 br	e-2842	31	4458.5	22423	1	e-515
4	4710.62	21228	4 br	e-1710	32	4452.83	22452	2	e-486
5	4680.10	21361	(00)	e-1577 ?	33	4443.10	22500	0	e-438
6	4652.01	21490	(1)	e-1448	34	4435.21	22541	2	e-397
7	4650.43	21497	4 or	e-1441	35	4429.91	22567	4	e-371
8	4645.10	21522	0	e-1416	36	4418.70	22625	0	f-371
9	4638.00	21552	0	e-1386	37	4409.9	22670	1	e-268 } m-2027 }
10	4634.34	21574	5	e-1364 } v-2948 }	38	4402.7	22707	0	e-231 ?
11	4624.50	21618	0	e-1320	39	4393.0	22757	1	e-181
12	4619.29	21640	0	f-1359	40	4383.5	22807	0	v-1709
13	4609.65	21688	4 br	e-1250	41	4325.0	23115	0	k-1585
14	4602.94	21719	2	e-1219	42	4296.2	23269	1	k-1446
15	4594.07	21761	8 bd	e-1177 } k-2944 }	43	4297.07	23285	2	k-1440
16	4591.73	21772	4	e-1166 } k-2933 }	44	4293.0	23287	0	k-1418
17	4584.27	21808	6	e-1130	45	4287.3	23318	0	k-1387
18	4572.47	21864	8 br	e-1071 } k-2841 }	46	4282.69	23345	4	k-1380
19	4567.92	21886	1	e-1052	47	4274.5	23368	0	k-1317
20	4563.48	21907	0	e-1031	48	4262.29	23455	4	k-1250
21	4550.58	21969	1	e-969	49	4256.06	23489	1	k-1216
22	4546.50	21989	0	e-949	50	4249.60	23525	1	k-1180
23	4539.20	22024	1	e-914	51	4247.4	23537	1	k-1168
24	4527.65	22080	1	e-858	52	4240.49	23576	4	k-1129
25	4523.31	22102	1	e-836	53	4229.57	23636	2	k-1069
26	4514.60	22144	0	e-794	54	4225.95	23655	2	k-1050
27	4510.6	22164	1	e-770	55	4222.03	23679	0	k-1026
28	4503.54	22199	6	e-739	56	4218.4	23699	0	k-739

TABLE IV—(Contd)

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
57	4211.42	23738	1	k-967	67	4132.06	24194	1	k-515
58	4207.90	23758	1	k-947	68	4127.05	24224	1	k-481
59	4203.8	23781	0	k-916	69	4119.55	24269	0	k-436
60	4191.44	23851	1	k-854	70	4112.58	24310	2	k-395
61	4188.45	23870	1	k-835	71	4109.8	24330	4 br	k-373 } o-2902 }
62	4180.50	23914	0	k-791	72	4092.0	24431	10 br	k-274 } p-2923 }
63	4176.91	23934	1	k-771	73	4085.7	24460	10 band	k-237 } q-2920 }
64	4171.41	23965	4	k-740	74	4077.8	24521	8 br	k-184 } p-2842 }
65	4143.42	24128	0	k-677					
66	4139.30	24152	1	k-553					

[br = broad, bd = broad and diffuse]

$\overline{\Delta\nu}$	182 (1)	270 (1)	372 (4)	396 (2)	437 (0)	483 (2)	515 (2)
ρ	.54	P	.56	.62	P	.45	.55
$\overline{\Delta\nu}$	553 (1)	660 (1)	739 (0)	770 (0)	792 (1)	831 (1)	856 (1)
ρ	D	P	.54	D	P	.56	
$\overline{\Delta\nu}$	915 (1)	948 (0)	968 (2)	1028 (0)	1051 (1)	1070 (2)	1129 (6)
ρ	.80	D	.71		P	P	53
$\overline{\Delta\nu}$	1167 (2)	1178 (2)	1217 (2)	1250 (4)	1318 (0)	1302 (6)	1386 (0)
ρ	D	D	.81	82	D	74	D
$\overline{\Delta\nu}$	1417 (0)	1441 (6)	1447 (0)	1710 (4 b)	2842 (8)	2930 (2)	2946 (2)
	D	.81		.61	.47	.57	57

TABLE V
Trans- β -Decalol (Solid)

No	λ	$\bar{\nu}$	I	Assignment
1	4223.57	23670	0	$k \rightarrow 1035$
2	4241 27	23571	0	$k \rightarrow 1134$
3	4262 39	23455	1	$k-1250$
4	4279 60	23360	1	$k-1345$
5	4296 82	23266	1	$k-1439$ $\nu-1250$)
6	4309.576	23198	0	$k-1507$
7	4570 07	21873	6	$k-2832$
8	4580 25	21827	(3)	$k-2878$
9	4588.41	21787	6	$k-2918$
10	4611 3	21680	0	$\nu-2836$
11	4629 1	21597	0	$\nu-2919$

$\overline{\Delta\nu} = 1035 (0), 1134 (0), 1250 (1), 1345 (1), 1439 (1), 1507 (0), 2834 (6), 2878 (3), 2918 (6)$

TABLE VI
Naphthalene

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
1	5029.44	19877	(4)	e-3061	23	4394.88	22747	(1) br	e-191
2	4679.85	21362	(5)	e-1578	24	2322.59	43128	(4)	k-1577
3	4669.12	21411	(4)	e-1527 ?	25	4320.57	23139	(2)	v-1377
4	4658.89	21458	(2)	k-3247 } v-3058 }	26	4314.65	23170	(0)	k-1535
5	4654.71	21478	(4)	e-1460	27	4301.07	23244	(3)	k-1461
6	4650.96	21495	(2)	e-1443	28	4295.74	23272	(1)	k-1433
7	4644.49	21525	(0)	e-1413 ?	29	4289.03	23309	(0)	k-1396
8	4636.99	21560	(15)	e-1378	30	4285.54	23328	(15)	k-1377
9	4625.92	21611	(2)	e-1327 } f-1378 }	31	4276.5	23381	(0)	k-1324
10	4618.96	21644	(3)	k-3061	32	4263.12	23450	(2)	k-1255
11	4614.57	21680	(2)	e-1258	33	4260.21	23467	(1)	k-1238
12	4607.29	21699	(1)	e-1239	34	4255.0	23495	(0)	k-1210
13	4601.2	21735	(0)	e-1203	35	4243.09	23561	(2)	k-1144
14	4586.04	21799	(2)	e-1139	36	4221.66	23681	(4)	k-1024
15	4562.05	21914	(5)	e-1024	37	4208.39	23755	(1)	k-945
16	4544.23	22000	(2)	e-938	38	4177.24	23932	(1)	k-773
17	4509.75	22168	(1)	e-770	39	4174.71	23946	(5)	k-759
18	4507.59	22178	(6)	e-760	40	4169.42	23977	(4)	k-728
19	4500.09	22212	(1)	e-726	41	4165.33	24001	(4)	v-511
20	4457.57	22427	(6)	e-511	42	4138.96	24154	(4)	p-3244
21	4446.46	22484	(0)	f-511	43	4131.89	24195	(6)	k-510
22	4434.60	22542	(1)	e-396 } m-3050 }	44	4124.36	24239	(4)	o-3054
					45	4114.92	24305	(1)	k-400 } p-3050 }
$\overline{\Delta\nu}$ P	191 (1) D	397 (1) D	511 (6) .65	727 (1) D	760 (6) .50	772 (1) P			
$\overline{\Delta\nu}$ P	941 (2) P	1024 (5) .55	1142 (2) .77	1206 (0) D	1239 (1) D	1258 (2) .77			
$\overline{\Delta\nu}$ P	1326 (1) P	1378 (15) .34	1406 ? .	1438 (2) D	1460 (4) .64				
$\overline{\Delta\nu}$ P	1530 (0) D	1576 (5) .53	3058 (4) .55	3244 (2) D					

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Trans- β Decalone



Tetralin



Decaline



Naphthalene



Tetralin



Indene



Decaline



Trans β -Decalone

State of Polarisation

THE NORMAL MODES AND FREQUENCIES OF THE SULPHUR MOLECULE.

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1 Normal Modes

THE model¹ assumed for sulphur molecule is that of a puckered octagon made up of two equal squares one turned through 45° with respect to the other. The planes of the two squares are parallel but not coincident. The atoms in the molecule occupy the corners of the puckered octagon. Let these atoms be denoted by the numbers 1, 2, 3, 4, 5, 6, 7, 8 as shown in Fig 1. The valence bonds are along (15), (25), (26), (36), (37), (47), (48), (81). Let XYZ be three rectangular axes through the centre of gravity of the molecule. X-axis is parallel to (86), Y-axis is parallel to (75) and Z-axis is perpendicular to the planes of the two squares. Let $2a$ be the side of a square and $2c$ be the distance between the two squares. The co-ordinates of the atoms, when referred to the above set of axes can be given in terms of a and c .

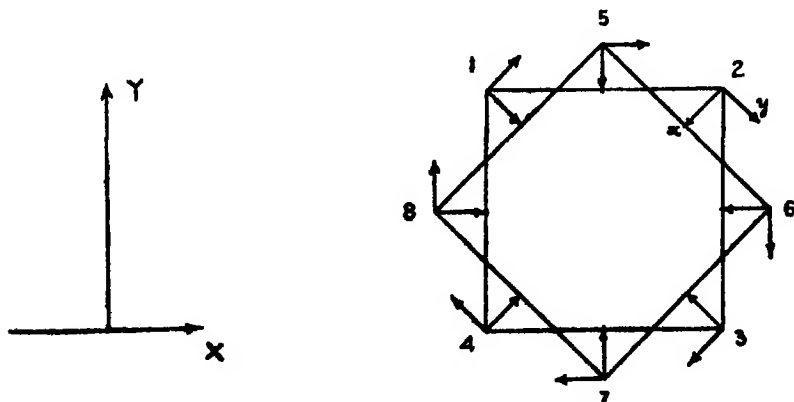


FIG. 1

In determining the potential energy and the kinetic energy of the molecule in any mode of oscillation, it will however be found useful to express the

¹ Warren, B. E., and Burwell, J. T., *Jour. Chem. Phys.*, 1935, 3, 6

co-ordinates of any atom referred to its equilibrium position as the origin. Accordingly the 24 co-ordinates q are shown in Fig. 1. x_i, y_i, z_i are the co-ordinates of the i th atom with its equilibrium position as the origin. x_i points towards the centre of the square in which the i th atom is situated and z_i is measured perpendicular to the plane of the square and is taken positively on the side opposite to the centre of gravity of the molecule. We assume that the vibrations of the molecule are of small amplitude compared to the inter-atomic distances. Accordingly the kinetic and potential energies are of the form

$$2 T = \sum m_i \dot{q}_i^2 \text{ and } 2 V = \sum a_{ij} q_i q_j \quad (1)$$

Expressions (1) can be simultaneously reduced to the form

$$2 T = \sum Q_k^2 \text{ and } 2 V = \sum \lambda_k Q_k^2, \quad (2)$$

where Q 's are linear combinations of the above q 's. The former are called the normal co-ordinates and each Q corresponds to a normal mode. The λ 's in the expression (2) are related to the normal frequencies ν_k by the equation

$$\lambda_k = 4 \pi^2 \nu_k^2 \quad (3)$$

If the coefficient λ of any normal co-ordinate Q is distinct from the other λ 's the corresponding normal mode is non-degenerate. On the other hand, if two or more Q 's have the same coefficient, the corresponding modes are degenerate and the degree of degeneracy is equal to the number of Q 's which have the same coefficient λ .

Following Wigner² and Tisza,³ Wilson⁴ obtained the normal modes of vibrations of benzene by group theoretical methods. In the present paper we apply the same method to sulphur.

The symmetry operations of the model assumed for sulphur fall into seven classes. E_1 the identity ($h_1 = 1$), S^1 rotation reflection by $\pm \frac{\pi}{4}$ about the fourfold axis of rotation ($h_2 = 2$), C^2 rotation by $\pm \frac{\pi}{2}$ about the fourfold axis ($h_3 = 2$), S^3 rotation reflection by $\pm \frac{3\pi}{4}$ about the fourfold axis ($h_4 = 2$), C^4 rotation by π about the fourfold axis ($h_5 = 1$), σ_v reflection in a plane perpendicular to the planes of the squares and containing a diagonal of one of the squares ($h_6 = 4$), C_2 rotation by π about an axis through the centre of gravity of the molecule and passing through the middle points of two opposite valencies such as (15) and (37) ($h_7 = 4$).

² *Göttinger Nachrichten*, 1930, 133.

³ *Z f Phys.*, 1933, 82, 48.

⁴ *Phys. Rev.*, 1934, 45, 706.

These operations form the group which may be given as a group of permutations on the 8 symbols 1, 2, 3, 4, 5, 6, 7, 8. The elements of this group are

E	
(15263748)	(14) (32) (75) (6) (8)
(18473625)	(24) (58) (76) (1) (3)
(1234) (5678)	(13) (65) (78) (2) (4)
(1432) (5876)	(27) (36) (18) (45)
(16453827)	(37) (28) (46) (15)
(17283546)	(38) (47) (25) (16)
(13) (24) (57) (68)	(26) (17) (35) (48)
(21) (34) (68) (7) (5)	

The above representation of the group is useful to obtain the normal co-ordinates but is not convenient for obtaining the conjugate classes of the group. By adopting the abstract form

$$P^2 = E, Q^2 = E, PQ = QP^{-1}$$

the conjugate classes and the multiplication table of the conjugate classes may be written out. The character table given below is deduced therefrom by the usual methods.*

Character Table and Selection Rules

	E	2 S ¹	2 C ²	2 S ³	C ⁴	4 σ _v	4 C ₂	n _i	n _c '	Raman	Infra red
A ₁	1	1	1	1	1	1	1	2	2	P	f
A ₂	1	1	1	1	1	-1	-1	1	0		
B ₁	1	-1	1	-1	1	1	-1	2	1	f	M ₁ = 0
B ₂	1	-1	1	-1	1	-1	1	1	1	f	f
E ₁	2	√2	0	-√2	-2	0	0	3	2	f	M ₂ = 0
E ₂	2	0	-2	0	2	0	0	3	3	D	f
E ₃	2	-√2	0	√2	-2	0	0	3	2	D	f
h _i	1	2	2	2	1	4	4				
X _f '	24	0	0	0	0	2	0				
h _i X _f '	24	0	0	0	0	8	0				
ψ _f '	18	0	-2	0	2	2	2				
h _i ψ _f '	18	0	-4	0	2	8	8				

* This character table may also be obtained directly from the work of Tisza. In a preliminary communication to the *Physical Review*, the selection rules and the number of Raman lines to be expected for this molecule have been reported by one of us. (*Phys. Rev.*, 1938, 53, 1015.)

In the above table P stands for a polarized Raman line, D stands for a depolarized Raman line and f stands for a forbidden line. M denotes the electric moment, h_j is the number of the symmetry operations under the class j and χ_j' is the character of the operation under the class j in respect of the original set of co-ordinates, ψ_j' is the character obtained after allowing for pure rotation and translation. We have the following relationships

$$\left. \begin{aligned} \chi_j' &= U_R (1 + 2 \cos \phi_R) \\ \psi_j' &= (U_R - 2) (1 + 2 \cos \phi_R) \end{aligned} \right\} \text{for operations R involving a pure rotation,}$$

and $\chi_j' = \psi_j' = U_R (-1 + 2 \cos \phi_R)$ for operations R involving rotation reflection

U_R denotes the number of invariant atoms and ϕ_R is the angle of rotation for the operation R. The number of modes n_i under the representation i is obtained with the help of the relation

$$n_i = \frac{1}{N} \sum_j h_j \chi_j' \chi_i$$

N is the order of the group and is 16 in this case. χ_j is the character of any operation under the class j in respect of the normal co-ordinates. The above relation includes pure rotations and translations. These may easily be excluded if we use alternatively

$$n_i' = \frac{1}{N} \sum_j h_j \psi_j' \chi_i$$

It now follows from the table that the normal modes under the various representations are given by

$$2 A_1 + A_2 + 2 B_1 + B_2 + 3 E_1 + 3 E_2 + 3 E_3$$

The coefficient of each letter denotes the number of modes coming under that representation. If pure rotations and translations are eliminated, we get

$$2 A_1 + B_1 + B_2 + 2 E_1 + 3 E_2 + 2 E_3$$

It therefore follows that if we use the normal co-ordinates, the determinant will split up into two linear factors (B_1, B_2), 5 quadratic factors of which two pairs are equal [$A_1, E_1(2), E_3(2)$] and 2 equal cubic factors [$E_2(2)$]. The selection rules in respect of the modes coming under each representation are also given in the above table for both Raman and infra-red spectra. These are obtained from Tisza and Wigner. We may now see that the Raman spectrum of molecular sulphur should be expected to contain two strong and well polarized lines and five depolarized lines. None of these will be represented in the infra-red absorption. These conclusions are not affected by the type of forces that we may postulate later. It may be noted here that a complete lack of correlation between Raman and infra-red spectra usually

arises in the cases of molecules having a centre of inversion as one of the elements of symmetry. The case of sulphur comes apparently under this type although it does not possess a centre of inversion.

2 Normal Co-ordinates

From the general theory of Wilson and Tisza, it is seen that every normal co-ordinate is associated with an irreducible representation of the group. The non-degenerate normal co-ordinates correspond to the irreducible representations of degree one (i.e., the irreducible representations in which the identity element has character one) and they can be obtained immediately from the character table. We take the most general linear expression for Q in the 24 co-ordinates x_i, y_i, z_i and if R is an operation of the group, $RQ = \lambda Q$ where λ is the character corresponding to the operation R . These relations in general determine Q . For example, if

$$Q = \sum_{i=1}^8 a_i x_i + \sum_{i=1}^8 b_i y_i + \sum_{i=1}^8 c_i z_i$$

is the normal co-ordinate corresponding to A_1 , it follows that

$$a_1 = a_2 = a_3 = a_4, \quad a_5 = a_6 = a_7 = a_8$$

and similar expressions in b 's and c 's by C_2 ,

$$a_1 = a_5, \quad b_1 = b_5, \quad c_1 = c_5 \text{ by } C_2$$

and $a_1 = a_3, \quad b_1 = -b_3, \quad c_1 = c_3$ by σ_v .

Hence it follows that the most general linear expression which corresponds to A_1 is

$$Q = a_1 (x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8) \\ + c_1 (z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8)$$

The normal co-ordinates $Q_x, Q_y, Q_z, Q_{\omega_x}, Q_{\omega_y}, Q_{\omega_z}$, which correspond respectively to translations and rotations of the molecule as a whole can be obtained directly. For the determination of the normal co-ordinates of degeneracy r , we take r linear expressions Q_1, Q_2, \dots, Q_r in the co-ordinates. If R is a group operation, we have

$$RQ_k = \lambda_{1k} Q_1 + \lambda_{2k} Q_2 + \dots + \lambda_{rk} Q_r \quad (k = 1, 2, \dots, r)$$

Using the fact that $\sum \lambda_{kk}$ is equal to the character of the group element R , we obtain certain relations which with the orthogonality relations between the coefficients of transformations (namely the sum of the product of coefficients of like terms in the expressions for two different normal co-ordinates is zero and the sum of the squares of the coefficients is unity for any normal co-ordinate) are in general sufficient to find a set of normal co-ordinates. For example, it follows from the character table that the normal

co-ordinates corresponding to E_2 will be of the form

$a_1 (x_1 + x_2 - x_3 - x_4) + a_2 (x_5 + x_7 - x_6 - x_8) + \text{similar expressions in } y\text{'s and } z\text{'s}$

Similarly those corresponding to E_1 and E_3 will be of the form

$a_1 (x_1 - x_2) + a_2 (x_3 - x_4) + a_3 (x_5 - x_7) + a_4 (x_6 - x_8) + \text{similar expressions in } y\text{'s and } z\text{'s}$

We find the degenerate Q 's now by using the orthogonality relations. It may be noted that the set of 24 normal co-ordinates thus obtained is not unique but it is always possible to obtain at least one such set

The following Q 's wherever they belong to a linear factor of the secular equation are the normal co-ordinates. In other cases they are functions which must be combined with one or more others in order to obtain the normal co-ordinates. Q_3, Q_4 indicate the normal co-ordinates with frequencies ν_3 and ν_4 . Q_1', Q_2' connected by a parenthesis indicate that two normal co-ordinates are obtained by forming two independent combinations of these with co-efficients which depend on the force constants. The corresponding frequencies ν_1 and ν_2 come under the class A_1 . Wherever the Q 's with dashes are connected by a parenthesis, similar combinations have to be formed in order to obtain the normal co-ordinates. Q_{aa}, Q_{bb} indicate two normal co-ordinates with the same frequency ν_a . Wherever Q 's with suffixes a and b occur, a degeneracy is implied

$$\begin{aligned}
 Q_x &= (x_1 - x_2) - (x_3 - x_4) - \sqrt{2} (x_5 - x_6) + (y_1 - y_2) + \\
 &\quad (y_3 - y_4) + \sqrt{2} (y_5 - y_7) \\
 Q_y &= - (x_1 - x_2) - (x_3 - x_4) - \sqrt{2} (x_5 - x_7) + (y_1 - y_2) - \\
 &\quad (y_3 - y_4) - \sqrt{2} (y_5 - y_6) \quad \left. \vphantom{\begin{aligned} Q_x \\ Q_y \end{aligned}} \right] - E_1 \quad (2) \\
 Q_3 &= x_1 + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 - x_8 \quad \quad \quad B_1 \\
 Q_{\omega_2} &= c [x_1 - x_2) + (x_3 - x_4) - \sqrt{2} (x_5 - x_7) - (y_1 - y_2) + \\
 &\quad (y_3 - y_4) - \sqrt{2} (y_5 - y_6) \\
 &\quad + a [\sqrt{2} (z_1 - z_2) + \sqrt{2} (z_3 - z_4) - 2 (z_5 - z_7)] \quad \quad \quad \left. \vphantom{\begin{aligned} Q_{\omega_2} \\ Q_{\omega_3} \end{aligned}} \right] - E_2 \quad (2) \\
 Q_{\omega_3} &= c [(x_1 - x_2) - (x_3 - x_4) + \sqrt{2} (x_5 - x_6) + (y_1 - y_2) + \\
 &\quad (y_3 - y_4) - \sqrt{2} (y_5 - y_7) + a [\sqrt{2} (z_1 - z_2) - \sqrt{2} (z_3 - z_4) \\
 &\quad + 2 (z_5 - z_6)] \quad \quad \quad \left. \vphantom{\begin{aligned} Q_{\omega_2} \\ Q_{\omega_3} \end{aligned}} \right] \\
 Q_{\omega_4} &= y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 \quad \quad \quad A_2 \\
 Q_1' &= x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 \\
 Q_2' &= x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 \quad \left. \vphantom{\begin{aligned} Q_1' \\ Q_2' \end{aligned}} \right] \dots 2 A_1 \\
 Q_3 &= x_1 + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 - x_8 \quad \quad \quad B_1 \\
 Q_4 &= y_1 + y_2 + y_3 + y_4 - y_5 - y_6 - y_7 - y_8 \quad \quad \quad B_2
 \end{aligned}$$

$$\left. \begin{aligned} Q'_{2a} &= a [(x_1 - x_3) - (x_2 - x_4) - \sqrt{2}(x_6 - x_8) - (y_1 - y_3) - \\ &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + c [-\sqrt{2}(z_1 - z_3) + \\ &\quad + \sqrt{2}(z_2 - z_4) + 2(z_6 - z_8)] \\ Q'_{6a} &= c [(x_1 - x_3) - (x_2 - x_4) - \sqrt{2}(x_6 - x_8) - (y_1 - y_3) - \\ &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + a [\sqrt{2}(z_1 - z_3) - \\ &\quad \sqrt{2}(z_2 - z_4) - 2(z_6 - z_8)] \\ Q'_{1b} &= a [(x_1 - x_3) + (x_2 - x_4) + \sqrt{2}(x_6 - x_8) + (y_1 - y_3) - \\ &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + c [-\sqrt{2}(z_1 - z_3) - \\ &\quad \sqrt{2}(z_2 - z_4) - 2(z_6 - z_8)] \\ Q'_{6b} &= c [(x_1 - x_3) + (x_2 - x_4) + \sqrt{2}(x_6 - x_8) + (y_1 - y_3) - \\ &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + a [\sqrt{2}(z_1 - z_3) + \sqrt{2}(z_2 - z_4) \\ &\quad + 2(z_6 - z_8)] \end{aligned} \right\} -2 E_1(2)$$

$$\left. \begin{aligned} Q'_{7a} &= x_1 + x_2 - x_3 - x_4 + z_5 + z_7 - z_6 - z_8 \\ Q'_{8a} &= x_5 + x_7 - x_6 - x_8 - z_1 - z_3 + z_2 + z_4 \\ Q'_{9a} &= y_1 + y_3 - y_2 - y_4 + y_5 + y_7 + y_6 - y_8 \\ Q'_{7b} &= x_5 + x_7 - x_6 - x_8 + z_1 + z_3 - z_2 - z_4 \\ Q'_{8b} &= x_1 + x_2 - x_3 - x_4 - z_5 - z_7 + z_6 + z_8 \\ Q'_{9b} &= y_1 + y_3 - y_2 - y_4 - y_5 - y_7 + y_6 + y_8 \end{aligned} \right\} 3 E_2(2)$$

$$\left. \begin{aligned} Q'_{10a} &= (x_1 - x_3) - (x_2 - x_4) + \sqrt{2}(x_6 - x_8) - (y_1 - y_3) - \\ &\quad (y_2 - y_4) + \sqrt{2}(y_5 - y_7) \\ Q'_{11a} &= a [(x_1 - x_3) - (x_2 - x_4) + \sqrt{2}(x_6 - x_8) + (y_1 - y_3) + \\ &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + c [-\sqrt{2}(z_1 - z_3) + \\ &\quad \sqrt{2}(z_2 - z_4) - 2(z_6 - z_8)] \\ Q'_{10b} &= (x_1 - x_3) + (x_2 - x_4) - \sqrt{2}(x_6 - x_8) + (y_1 - y_3) - \\ &\quad (y_2 - y_4) + \sqrt{2}(y_5 - y_7) \\ Q'_{11b} &= a [(x_1 - x_3) + (x_2 - x_4) - \sqrt{2}(x_6 - x_8) - (y_1 - y_3) + \\ &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + c [-\sqrt{2}(z_1 - z_3) - \\ &\quad \sqrt{2}(z_2 - z_4) + 2(z_6 - z_8)] \end{aligned} \right\} 2 E_3(2)$$

Each of the above equations should be multiplied by the reciprocal of the sum of the squares of the coefficients of q 's occurring in that equation.

3 Modes of Oscillation

All the seventeen modes of oscillation are diagrammatically represented below. Those corresponding to pure rotations and translations may easily be identified.

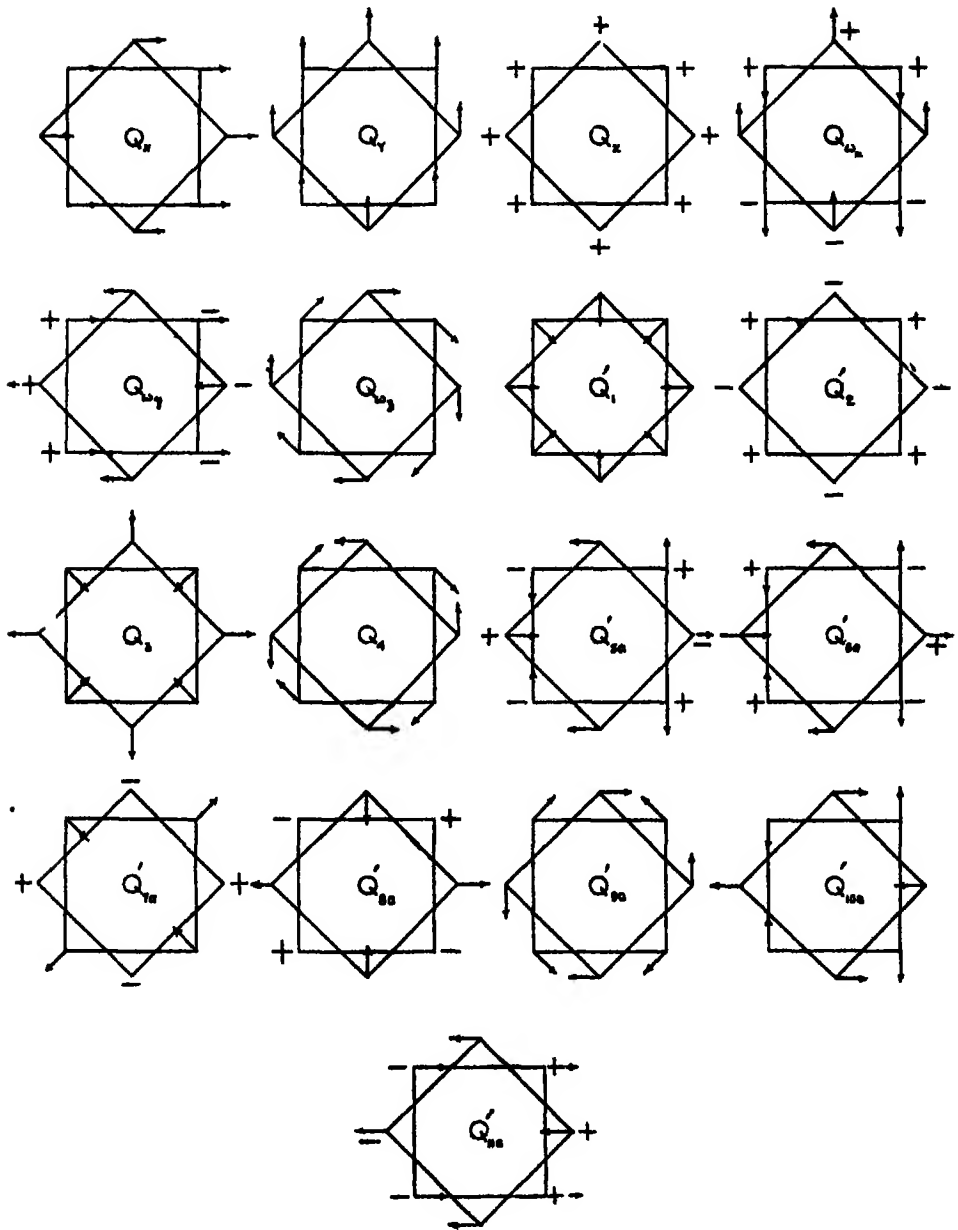


FIG 2

4 Potential Energy Function

We will now form the potential energy function in terms of three types of forces, namely, the primary valence forces, the directed valence forces, and the repulsive forces between the distant atoms which are not directly bonded. K_1 , K_2 and K_3 denote the respective force constants. The potential energy is the sum of three terms V_1 , V_2 and V_3 given by

$$2 V_1 = K_1 [(\Delta R_{12})^2 + (\Delta R_{23})^2 + (\Delta R_{34})^2 + (\Delta R_{35})^2 + (\Delta R_{37})^2 \\ + (\Delta R_{47})^2 + (\Delta R_{48})^2 + (\Delta R_{18})^2],$$

where ΔR_{ij} is the variation of the length of the valence bond connecting the i th and the j th atoms

$$2 V_2 = K_2 [(\Delta \phi_1)^2 + (\Delta \phi_2)^2 + (\Delta \phi_3)^2 + (\Delta \phi_4)^2 + (\Delta \phi_5)^2 + (\Delta \phi_6)^2 \\ + (\Delta \phi_7)^2 + (\Delta \phi_8)^2],$$

where $\Delta \phi_r$ is the variation of the angle between the two valence bonds at the r th atom

$$2 V_3 = K_3 [(\Delta S_{12})^2 + (\Delta S_{23})^2 + (\Delta S_{34})^2 + (\Delta S_{41})^2 \\ + (\Delta S_{56})^2 + (\Delta S_{67})^2 + (\Delta S_{78})^2 + (\Delta S_{85})^2],$$

where ΔS_{ij} is the variation of the distance of the i th and the j th atoms which are not directly bonded

5 Calculation of the Frequencies

The coefficient of any co-ordinate in the expressions for the Q 's gives the component along that co-ordinate direction. These coefficients are proportional to the amplitudes of the motions of the atoms in the corresponding modes of vibration. We can therefore find the potential and kinetic energies of the molecule for any given mode and then obtain the frequencies, using Lagrange's equations of motion.

In the case of frequencies coming from a linear factor of the secular equation, the position of the atoms during an oscillation can be completely described by giving the value of one co-ordinate. For example,

$$Q_1 = x_1 + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 - x_8$$

is the normal co-ordinates corresponding to B_1 and if in this mode of oscillation the amplitude of vibration is δ , each of the atoms 1, 2, 3, 4 undergoes a displacement δ towards the centre of the square (1234) and each of the atoms 5, 6, 7, 8 undergoes displacement δ away from the centre of the square (5678). The various lengths and angles in the displaced positions may easily

be evaluated and the variations written as

$$\Delta R_{15} = \Delta R_{25} = \Delta R_{35} = \Delta R_{37} = \Delta R_{47} = \Delta R_{48} = \Delta R_{18} = 0.$$

$$\Delta \phi_1 = \Delta \phi_2 = \Delta \phi_3 = \Delta \phi_4 = \frac{2\sqrt{2}a\delta}{R^2 \sin \phi}$$

$$\Delta \phi_5 = \Delta \phi_6 = \Delta \phi_7 = \Delta \phi_8 = -\frac{2\sqrt{2}a\delta}{R^2 \sin \phi}$$

ϕ is the angle between the two valence bonds at any atom in the equilibrium position

$$\Delta S_{12} = \Delta S_{23} = \Delta S_{34} = \Delta S_{41} = -\sqrt{2}\delta$$

$$\Delta S_{56} = \Delta S_{67} = \Delta S_{78} = \Delta S_{85} = \sqrt{2}\delta$$

Hence

$$2V_1 = 0 \quad 2V_2 = \frac{64a^2\delta^2}{R^4 \sin^2 \phi} K_2, \quad 2V_3 = 16K_2\delta^2$$

and the total potential energy is given by

$$2V = \frac{64a^2\delta^2}{R^4 \sin^2 \phi} K_2 + 16K_2\delta^2$$

The kinetic energy is given by

$$2T = 8m \left(\frac{d\delta}{dt} \right)^2.$$

The equation of motion is

$$m \cdot \frac{d^2\delta}{dt^2} + \left(\frac{8K_2a^2}{R^4 \sin^2 \phi} + 2K_2 \right) \delta = 0$$

We now obtain λ_2 as

$$\lambda_2 = \frac{1}{m} \left(\frac{8K_2a^2}{R^4 \sin^2 \phi} + 2K_2 \right).$$

ν_2 follows from the relation (3)

Similarly we find the other frequency relating to the second linear factor of the secular equation.

In the case of frequencies coming from quadratic or cubic factors of the secular equation, the treatment is slightly different. We have to take two different amplitudes corresponding to the two Q 's giving the frequencies for the quadratic and similarly three for the cubic. We will work out the case of a quadratic factor (E_2) as an example. We have

$$Q'_{100} = (x_1 - x_2) - (x_3 - x_4) + \sqrt{2}(x_5 - x_6) - (y_1 - y_2) - (y_3 - y_4) + \sqrt{2}(y_5 - y_6)$$

$$Q'_{11s} = a [(x_1 - x_2) - (x_3 - x_4) + \sqrt{2}(x_5 - x_6) + (y_1 - y_2) + (y_3 - y_4) - \sqrt{2}(y_5 - y_6)]$$

$$+ c [-\sqrt{2}(z_1 - z_2) + \sqrt{2}(z_3 - z_4) - 2(z_5 - z_6)]$$

as the normal co-ordinates giving ν_{10} and ν_{11} . If the amplitude of vibration is δ in the first mode, all the atoms undergo a displacement equal to $\sqrt{2} \delta$ in the directions shown in the mode Q'_{10a} . If the amplitudes of vibration is β in the second mode, atom 1 moves through a distance $\sqrt{2} a\beta$ in the direction (12) and a distance $-\sqrt{2} c\beta$ in a direction perpendicular to the square (1234). The displacements in respect of the other atoms may be similarly obtained. The co-ordinates of the atoms in the displaced positions for the combined mode are given in the following table

Atom	X co-ordinate	Y co-ordinate	Z co-ordinate
1	$-a + \sqrt{2} a\beta$	$a - \sqrt{2} \delta$	$c - \sqrt{2} c\beta$
5	$\sqrt{2} \delta - \sqrt{2} a\beta$	$\sqrt{2} a$	$-c$
2	$a + \sqrt{2} a\beta$	$a + \sqrt{2} \delta$	$c + \sqrt{2} c\beta$
6	$\sqrt{2} a - \sqrt{2} \delta - \sqrt{2} a\beta$	0	$-c + \sqrt{2} c\beta$
3	$a + \sqrt{2} a\beta$	$-a - \sqrt{2} \delta$	$c + \sqrt{2} c\beta$
7	$\sqrt{2} \delta - \sqrt{2} a\beta$	$-\sqrt{2} a$	$-c$
4	$-a + \sqrt{2} a\beta$	$-a + \sqrt{2} \delta$	$c - \sqrt{2} c\beta$
8	$-\sqrt{2} a - \sqrt{2} \delta - \sqrt{2} a\beta$	0	$-c - 2 c\beta$

We evaluate the variations in lengths and angles as before and obtain

$$\Delta R_{15} = -\Delta R_{25} = -\Delta R_{37} = \Delta R_{47} = \frac{2a\delta - 2\sqrt{2}(a^2 + c^2)\beta}{R}$$

$$\Delta R_{36} = \Delta R_{26} = -\Delta R_{48} = -\Delta R_{18} \\ = \frac{2(\sqrt{2} - 2)\beta(a^2 + c^2) + 2(\sqrt{2} - 1)a\delta}{R}$$

$$\Delta \phi_5 = \Delta \phi_7 = 0$$

$$\Delta \phi_2 = \Delta \phi_3 = -\Delta \phi_1 = -\Delta \phi_4$$

$$= \frac{-2\sqrt{2}a\delta + (4 - 4\sqrt{2})(a^2 + c^2)\beta + \cos \phi [(4 - 2\sqrt{2})a\delta + (4 - 4\sqrt{2})(a^2 + c^2)\beta]}{R^2 \sin \phi}$$

$$\Delta \phi_6 = \Delta \phi_8 = \sqrt{2} \Delta \phi_1$$

$$\Delta S_{12} = \Delta S_{34} = 0; \Delta S_{23} = -\Delta S_{14} = 2\sqrt{2}\delta, \Delta S_{56} = \Delta S_{67} \\ = -\Delta S_{78} = -\Delta S_{85} = 2\delta$$

Hence the potential energy is

$$2V = \frac{4K_1}{R^2} [(16 - 8\sqrt{2})a^2\delta^2 + \beta^2(a^2 + c^2)(32 - 16\sqrt{2}) \\ + a\delta\beta(a^2 + c^2)(32 - 32\sqrt{2})] \\ + \frac{8K_2}{R^4 \sin^2\phi} [8(a + 2b\cos\phi)^2\delta^2 + 16p^2(1 - \cos\phi)^2\beta^2 \\ + 16\sqrt{2}p(a + 2b\cos\phi)(1 - \cos\phi)\beta\delta] \\ + 32K_3\delta^2,$$

where $p = (\sqrt{2} - 1)(a^2 + c^2)$

The total kinetic energy is given by

$$2T = 16m \left[\left(\frac{d\delta}{dt} \right)^2 + (a^2 + c^2) \left(\frac{d\beta}{dt} \right)^2 \right].$$

The corresponding determinant is easily obtained and is given in the next page. The two roots of this determinant give λ_{10} and λ_{11} from which we obtain ν_{10} and ν_{11} . Other frequencies are similarly calculated. The equations in respect of all the eleven modes of oscillation are listed below. k_1, k_2, k_3 used in these determinants are respectively identical with K_1, K_2, K_3 used in the rest of the paper.

λ_1 and λ_2 are the roots of

$$\begin{vmatrix} \frac{16b^2k_1}{R^2} + \frac{k_2}{\sin^2\phi} \left(\frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4} \right)^2 & -\frac{16bck_1}{R^2} + \frac{16a^2ck_2}{R^4 \sin^2\phi} \left(\frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4} \right) \\ -\frac{16bck_1}{R^2} + \frac{16a^2ck_2}{R^4 \sin^2\phi} \left(\frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4} \right) & \frac{16c^2k_1}{R^2} + \frac{16a^4c^2k_2}{R^8 \sin^2\phi} - m\lambda \end{vmatrix} = 0$$

$$\lambda_3 = \frac{1}{m} \left(\frac{8k_3a^2}{R^4 \sin^2\phi} + 2k_3 \right)$$

$$\lambda_4 = \frac{4k_1a^2}{mR^2}$$

λ_5 and λ_6 are the roots of

$$\begin{aligned}
 & \frac{[a^4(4-2\sqrt{2})+c^4(8+4\sqrt{2})+8a^2c^2]}{R^2} + \frac{k_1}{R^2} \\
 & + \frac{2[2a^2-(1-\cos\phi)q]^2k_2}{R^4\sin^2\phi} + \frac{2a^2k_3-m\lambda(a^2+c^2)}{R^4\sin^2\phi} \\
 & + \frac{k_1ac}{R^2} [-2\sqrt{2}a^2-4(\sqrt{2}+1)c^2] \\
 & + \frac{2k_2[2a^2-(1-\cos\phi)q][2ac+(1-\cos\phi)r]+2ack_3}{R^4\sin^2\phi} \\
 & + \frac{2a^2c^2(2+\sqrt{2})k_1}{R^2} + \frac{2[2ac+(1-\cos\phi)r]^2k_2}{R^4\sin^2\phi} \\
 & + 2c^2k_3-m\lambda(a^2+c^2) \\
 & = 0
 \end{aligned}$$

λ_r, λ_s and λ_o are the roots of

$$\begin{aligned}
 & \frac{2a^2k_1}{R^2} + \frac{4(a\cos\phi+2b)^2k_2}{R^4\sin^2\phi} \\
 & + 2k_3-m\lambda \\
 & - \frac{2a(b+c)k_1}{R^2} \\
 & + \frac{4(b+c)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} \\
 & + \frac{4(b^2+c^2)k_1}{R^2} \\
 & + \frac{8(1-\cos\phi)^2(b^2+c^2)k_2}{R^4\sin^2\phi} - m\lambda \\
 & - \frac{2a(c-b)k_1}{R^2} \\
 & + \frac{4(c-b)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} \\
 & - \frac{2a(c-h)k_1}{R^2} \\
 & + \frac{4(c-b)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} \\
 & = 0
 \end{aligned}$$

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$$\begin{aligned}
 & \frac{4(b^2+c^2)k_1}{R^2} \\
 & + \frac{8(1-\cos\phi)^2(b^2+c^2)k_2}{R^4\sin^2\phi} - m\lambda
 \end{aligned}$$

λ_{10} and λ_{11} are the roots of

$$\frac{(4-2\sqrt{2})a^2k_1}{R^2} + \frac{4(a+2b\cos\phi)^2k_2}{R^4\sin^2\phi} \left| \begin{array}{l} \frac{(1-4\sqrt{2})a(a^2+c^2)k_1}{R^2} \\ + \frac{4\sqrt{2}p(a+2b\cos\phi)(1-\cos\phi)k_2}{R^4\sin^2\phi} \end{array} \right| = 0$$

$$\frac{(4-4\sqrt{2})a(a^2+c^2)k_1}{R^2} + \frac{4\sqrt{2}p(a+2b\cos\phi)(1-\cos\phi)k_2}{R^4\sin^2\phi} \left| \begin{array}{l} \frac{(8-4\sqrt{2})(a^2+c^2)^2k_1}{R^2} \\ + \frac{8p^2(1-\cos\phi)^2k_2}{R^4\sin^2\phi} - m\lambda(a^2+c^2) \end{array} \right|$$

In the above equations

$$2b = (\sqrt{2} - 1)a$$

$$p = (\sqrt{2} - 1)(a^2 + c^2)$$

$$-\cos\phi = \frac{2(\sqrt{2} - 1)a^2 - 4c^2}{R^2}$$

$$q = (2 + 2\sqrt{2})c^2 + \sqrt{2}a^2$$

$$r = (2 + \sqrt{2})ac$$

6 Summary

The normal modes and frequencies of the sulphur molecule have been worked out on the assumption that the eight atoms in the molecule occupy the corners of a puckered octagon. There are eleven modes of which four are single and seven are doubly degenerate. Two of the former type and five of the latter type are Raman active. One is inactive in both Raman and infra-red spectra and the others are active only in infra-red absorption. The result obtained in respect of the Raman effect of sulphur are in agreement with the above conclusions.

Detailed expressions are derived for the normal frequencies by postulating three types of forces, namely, primary valence, directed valence and repulsive forces.

RAMAN SPECTRUM AND SPECIFIC HEAT OF SULPHUR.

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1. Frequencies and Force Constants

THE equations relating to all the eleven vibrational frequencies that are to be expected of the sulphur molecule when it is regarded as a puckered octagon have been given in a previous paper *. Only seven of these are active in Raman effect and three others are active in infra-red absorption. There is one frequency which is inactive in both Raman effect and infra-red absorption. None of the Raman frequencies are to be expected in the infra-red absorption and *vice versa*. Of the seven frequencies that are to be expected in Raman effect, two come under the total symmetric class (A_1) and should accordingly give rise to two strong and well polarised Raman lines. The Raman spectrum of sulphur¹ does exhibit two strong and well polarised lines at 470 and 216 and these may at once be identified with ν_1 and ν_2 in the notation of the paper already cited. We may now substitute these in the quadratic for λ_1 and λ_2 and obtain approximate values for K_1 and K_2 if we provisionally assume a zero value for K_3 . If these are substituted in the expression for ν_7 , a value which is in the neighbourhood of 243 is obtained for it. Thus, ν_1 , ν_2 and ν_7 are respectively identified with 470, 216 and 243. Using these values, K_1 , K_2 and K_3 may be obtained as $K_1 = 2.309 \times 10^6$ dynes/cm, $K_2 = 0.903 \times 10^{-11}$ dynes cm/radian, $K_3 = 0.0665 \times 10^6$ dynes/cm. K_1 , K_2 and K_3 respectively represent the force constants in respect of the primary valence, directed valence and repulsive forces. This set of force constants is used to calculate all the frequencies. The values thus calculated are compared below in Table I with the observed values. Data in respect of infra-red absorption are taken from Barnes². A better agreement may have been obtained by altering the constants slightly but the labour involved will be considerable and it is therefore not attempted.

The dimensions of the molecule are taken from the work of Warren and Burwell.

* See preceding paper in this *Journal*.

¹ C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, (A), 1937, 4, 345.

² *Phys. Rev.*, 1932, 39, 562.

TABLE I *Normal Frequencies of Sulphur*

Class	Frequency calculated cm ⁻¹	Frequency observed cm ⁻¹	
		Infra-red	Raman
A ₁	481	<i>f</i>	470 (P)
	197	<i>f</i>	216 (P)
B ₁	255	267 (w)	<i>f</i>
B ₂	557	<i>f</i>	<i>f</i>
E ₁	481	465 (st)	<i>f</i>
	181	200 (st)	<i>f</i>
E ₂	243	<i>f</i>	243
	456	<i>f</i>	434 (D)
	122	<i>f</i>	152 (D)
E ₃	542	<i>f</i>	114 (?)
	211	<i>f</i>	185

In the above Table *f* stands for forbidden, D for a depolarised and P for a well-polarised Raman line. The available polarisation data in respect of Raman lines are included. The intensities of infra-red absorption are indicated in brackets. It may be noted that only two well-polarised Raman lines are observed and of the other five, data available show that two are depolarised. These results are in perfect agreement with what may be expected of the proposed model. All the observed Raman frequencies except the one at 88 have been listed in the above table. Venkateswaran has given good reasons to show that this low frequency is characteristic of the lattice and hence need not be considered here. There is fair agreement between the calculated and observed frequencies in all cases except the one at 542. No line is reported in the neighbourhood of 542 but a weak line has been recorded by Venkateswaran at 114. It is possible that this line at 114 also belongs to the lattice and not to the molecule. In such a case another Raman line in the neighbourhood of 542 is to be expected. Of the various infra-red absorption maxima recorded by Barnes, the two strong ones at 465 and 200 are satisfactorily explained and these are to be regarded as fundamentals. Another weak absorption at 267 is also presumably a fundamental. Other absorption maxima have to be explained as combination tones or overtones.

The relatively small value of K_2 shows that the primary valence and the directed valence forces are the more important ones. This inference is in agreement with the observations of Badger.³ The value of K_1 obtained in this molecule suggests that the adjacent sulphur atoms are bound to each other by single bonds. Utilising this value, we may calculate the S-S frequency with the help of the relation $\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$, where μ is the reduced mass. When expressed in wave-numbers, this comes out as 496 and compares well with 512 observed in disulphides containing this group.⁴ If we take the force constant for S = S as twice the value of K_1 , i.e., 4.618×10^5 dynes/cm, the corresponding frequency comes out as 702 and agrees well with the vibrational frequency 724 of sulphur vapour obtained from the band spectrum data.

2 Specific Heat of Sulphur

The specific heat at any temperature consists of two parts arising respectively from the rotational and translational motions and the internal vibrations. Following the recent work of Lord, Ahlberg and Andrews,⁵ we will assume that the former is represented by $2D\left(\frac{\theta}{T}\right)$, where D is the Debye function and θ is the mean effective characteristic temperature in respect of longitudinal and torsional elastic waves. The value of this is assumed to be 74.5 for sulphur and it corresponds to $\nu = 52 \text{ cm}^{-1}$. The exact relationship of θ to the observed Raman frequencies in the region of lattice oscillations is not discussed here. The eleven internal vibration frequencies are taken as 152 (2), 185 (2), 200 (2), 216 (1), 243 (2), 267 (1), 434 (2), 465 (2), 470 (1), 542 (2), 557 (1), and an Einstein function is associated with each one of them. The number in parenthesis represents the degree of degeneracy in each case. The sum of all the Einstein functions is the contribution of the latter type to the specific heat. The specific heat thus calculated is compared with the observed specific heat⁶ at different temperatures in Table II.

Satisfactory and general agreement between the observed and calculated specific heats is noticed. At temperatures higher than 50° K the observed value is always somewhat larger than the calculated one. This may be due to the fact that the former refers to constant pressure whereas the calculations refer only to constant volume. The recent work of Sirkar and

³ *Jour. Chem. Phys.*, 1935, 3, 710

⁴ S. Venkateswaran, *Ind Jour. Phys.*, 1931, 6, 5

⁵ *Jour. Chem. Phys.*, 1937, 5, 649.

⁶ Values are taken from *I.C.T.*, 5, Nernst, *Ann. d. Phys.*, 1911, 36, 395.

TABLE II *Specific Heat of Sulphur.*

Temperature K	$2D \left(\frac{74.5}{T} \right)$	Vibrational contribution	C_v Specific heat calc (total)	C_p Observed
10	1.96	0	1.96	2.48
20	6.50	0.01	6.51	5.76
30	8.94	0.23	9.17	9.20
40	10.08	1.02	11.10	11.26
50	10.70	2.38	13.08	14.16
60	11.04	4.08	15.12	16.64
70	11.26	5.88	17.14	19.04
80	11.40	7.61	19.01	21.44
90	11.50	9.40	20.90	23.52
100	11.58	11.04	22.62	25.60
150	11.76	17.95	29.71	32.88
200	11.82	22.90	34.72	37.52
250	11.86	26.27	38.13	41.04
300	11.88	28.58	40.46	44.56

Gupta⁷ may be referred to in this connection. Their calculations are however incomplete as they have not taken account of all the vibrational frequencies.

3 Summary

Using the expressions derived by us in an earlier paper for the vibrational frequencies of the sulphur, the force constants K_1 , K_2 and K_3 referring respectively to primary valence, directed valence and repulsive forces are evaluated. The values obtained are $K_1 = 2.309 \times 10^8$ dynes/cm, $K_2 = 0.903 \times 10^{-11}$ dynes cm/radian and $K_3 = 0.06665 \times 10^8$ dynes/cm. The frequencies calculated on the basis of these constants are compared with the observed Raman lines and infra-red absorption maxima and satisfactory agreement obtained.

The specific heat of sulphur is represented as the sum of a Debye function and a number of Einstein functions associated with the various normal frequencies. The calculated values compare favourably with the observed specific heats.

⁷ *Ind. Journ. Phys.*, 1938, 12, 143.

THE NORMAL FREQUENCIES OF PHOSPHORUS (P₄).

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1 Character Table

THE structure assumed for the P₄ molecule is that of a regular tetrahedron, the atoms being situated at its corners. Evidence from various fields of investigation is strongly in favour of such a structure and hence other possibilities are not considered here. The model belongs to the tetrahedral point group T_d. The character table and the selection rules appropriate to this group are given below.

T_d Group.

T _d	E	8 C ₃	3 C ₂	6 σ	6 S ₄	n _i	n' _i	Raman	Infra red
A ₁	1	1	1	1	1	1	1	P	f
A ₂	1	1	1	-1	-1	0	0	.	.
E	2	-1	2	0	0	1	1	D	f
F ₁	3	0	-1	-1	1	1	0		
F ₂	3	0	-1	1	-1	2	1	D	active
h _i	1	8	3	6	6				
X _i '	12	0	0	2	0				
h _i X _i '	12	0	0	12	0				
ψ _i	6	0	2	2	0				
h _i ψ _i '	6	0	6	12	0				

The notation employed is the same as that already given in earlier papers by us in these *Proceedings*. It is seen from the table that we should expect three normal frequencies one of them being single, one doubly degenerate and one triply degenerate. All the three are active in Raman effect whereas only one is active in infra-red absorption. Of the three lines that are to be accordingly expected in Raman effect, the single frequency coming under the total symmetric class A₁ should be perfectly polarised and the remaining two

being degenerate should be completely depolarised. The experimental results¹ in respect of the Raman effect in phosphorus are in entire agreement with the above conclusions.

2 Normal Co-ordinates and Modes

The principal axes, X, Y, Z, are shown in Fig. 1. They are obtained by joining the middle points of opposite sides of the tetrahedron and the positive directions are indicated by the letters X, Y, Z. The co-ordinates of each

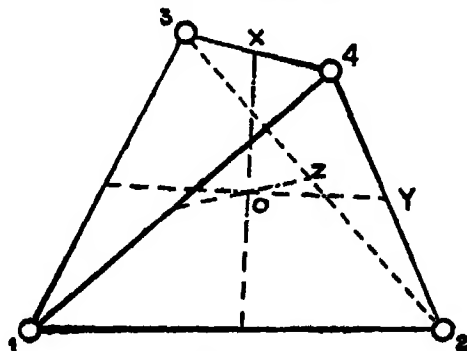


FIG. 1

atom in any mode of oscillation are expressed with respect to a parallel co-ordinate system with the equilibrium position of the atom as the origin. The normal co-ordinates derived from the character table and the orthogonality relations are given below. The first six relate to pure translations and rotations.

$$\left. \begin{aligned} Q_x &= x_1 + x_2 + x_3 + x_4 \\ Q_y &= y_1 + y_2 + y_3 + y_4 \\ Q_z &= z_1 + z_2 + z_3 + z_4 \end{aligned} \right\} \dots \dots \dots F_3 \quad (3)$$

$$\left. \begin{aligned} Q_{\omega x} &= y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4 \\ Q_{\omega y} &= x_1 - x_2 - x_3 + x_4 + z_1 + z_2 - z_3 - z_4 \\ Q_{\omega z} &= x_1 - x_2 + x_3 - x_4 + y_1 + y_2 - y_3 - y_4 \end{aligned} \right\} \dots \dots F_1 \quad (3)$$

$$\left. \begin{aligned} Q_1 &= x_1 + x_2 - x_3 - x_4 + y_1 - y_2 + y_3 - y_4 + z_1 - z_2 - z_3 + z_4 \\ Q_{2a} &= y_1 - y_2 + y_3 - y_4 - z_1 + z_2 + z_3 - z_4 \\ Q_{2b} &= 2x_1 + 2x_2 - 2x_3 - 2x_4 - y_1 + y_2 - y_3 + y_4 - z_1 + z_2 + z_3 - z_4 \end{aligned} \right\} E \quad (2)$$

$$\left. \begin{aligned} Q_{3a} &= y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4 \\ Q_{3b} &= x_1 - x_2 - x_3 + x_4 + z_1 + z_2 - z_3 - z_4 \\ Q_{3c} &= x_1 - x_2 + x_3 - x_4 + y_1 + y_2 - y_3 - y_4 \end{aligned} \right\} \dots \dots F_2 \quad (3)$$

¹ S. Bhagavantam, *Ind. Jour. Phys.*, 1930, 5, 35, C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, 1937, 4, 345.

The modes of oscillation in respect of Q_1 , Q_{2a} and Q_{3a} are shown diagrammatically in Fig 2. In the case of Q_1 , the actual displacements which each atom undergoes are shown. In the other two modes, the components

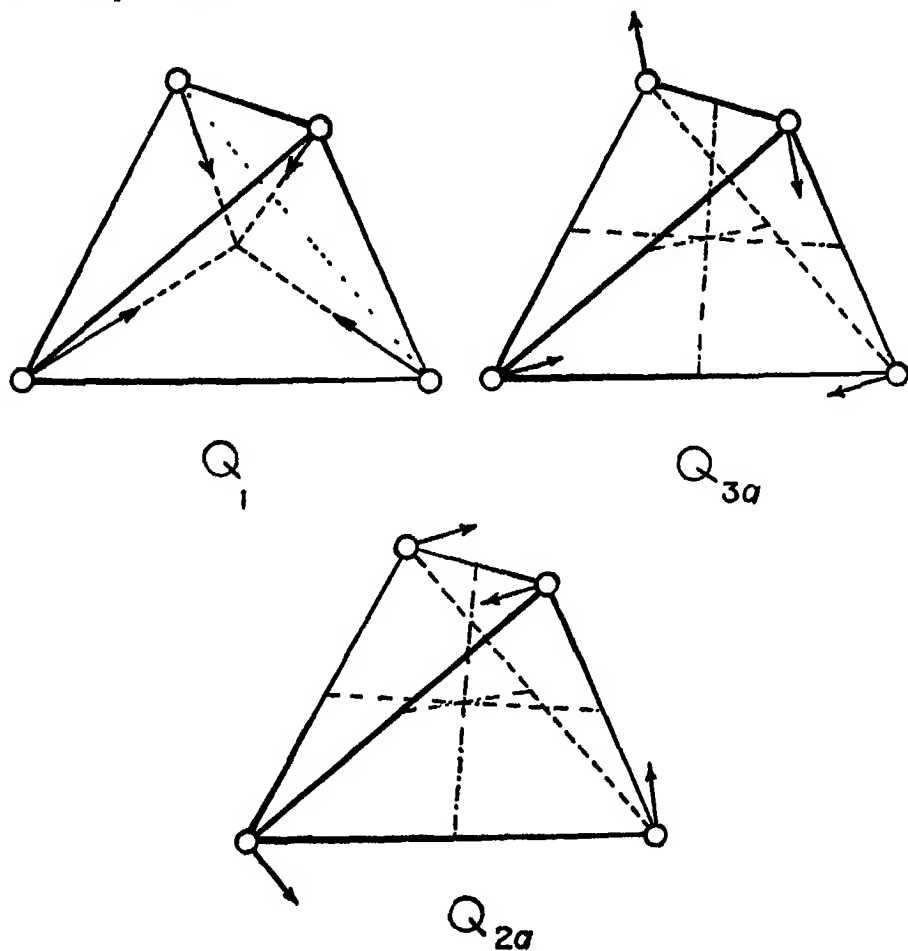


FIG. 2

of the displacements of each atom along the three axes are shown separately. The representation follows closely the method adopted by Born² in connection with AB_4 molecules

3 Potential Energy Function and Normal Frequencies

The potential energy function chosen involves primary valence and directed valence forces and is given by:

² *Optik*, Julius Springer, 1933.

$$\begin{aligned}
2V = & K_1 [(\Delta R_{12})^2 + (\Delta R_{13})^2 + (\Delta R_{14})^2 + (\Delta R_{23})^2 \\
& + (\Delta R_{24})^2 + (\Delta R_{34})^2] \\
& + K_2 [(\Delta \phi_{123})^2 + (\Delta \phi_{214})^2 + (\Delta \phi_{314})^2 + (\Delta \phi_{124})^2 + (\Delta \phi_{134})^2 \\
& + (\Delta \phi_{234})^2 + (\Delta \phi_{132})^2 + (\Delta \phi_{124})^2 + (\Delta \phi_{234})^2 + (\Delta \phi_{142})^2 \\
& + (\Delta \phi_{143})^2 + (\Delta \phi_{243})^2]
\end{aligned}$$

where R_{ij} denotes the distance between the i th and the j th atoms and ϕ_{ijk} is the angle between the two valence bonds ij and jk . In all the three normal modes the variations ΔR and $\Delta \phi$ are then calculated in the usual manner and the potential energies evaluated. The corresponding kinetic energies are written down and the following relations obtained from the equations of motion

$$\begin{aligned}
\lambda_1 &= \frac{4K_1}{m} \\
\lambda_2 &= \frac{1}{m} \left[K_1 + \frac{6K_2}{R^2} \right] \\
\lambda_3 &= \frac{1}{m} \left[2K_1 + \frac{8K_2}{R^2} \right] \quad . \quad (1)
\end{aligned}$$

where R is the length of each valence bond and m is the mass of the phosphorus atom. ν_1 , ν_2 and ν_3 corresponding respectively to the representations A_1 , E and F_2 may now easily be obtained from the relation $\lambda = 4\pi\nu^2$. Assuming ν_1 and ν_2 as 606 and 468 cm^{-1} respectively, we obtain ν_3 directly from the relations (1) as 344. This compares well with the observed value, namely 363. We may also evaluate K_1 and K_2 if we assign a value for R . We assume³ that $R = 2.21 \times 10^{-8}$ cm and obtain $K_1 = 1.68 \times 10^8$ dynes/cm and $K_2 = 0.396 \times 10^{-11}$ dynes cm/radian.

We can utilise the value of K_1 thus obtained for calculating the frequency that is to be expected of a $\text{P} = \text{P}$ molecule. Taking the force constant appropriate to this case as $3K_1$, the oscillation frequency may be evaluated as 742. This may be compared with the experimental value 779 obtained from band spectra.

4. Specific Heat of Phosphorus.

The specific heat of phosphorus is calculated at 9° C. by assigning 12 calories on account of the Debye functions and evaluating the three Einstein functions corresponding to the observed normal frequencies 606, 468, 363. The result obtained is 19.8 calories whereas the experimental value available⁴

³ Maxwell, Hendricks and Mosley, *Jour. Chem. Phys.*, 1935, 3, 699.

⁴ The value is taken from *Landolt Bornstein Tabellen* and is due to Ewald.

for yellow phosphorus at 9° C is 22.0 calories. Experimental data in respect of the specific heat of phosphorus at different temperatures is not available.

5 Summary

Assuming a potential energy function based on primary valence and directed valence forces, expressions are obtained by group theoretical methods for the normal frequencies of the tetrahedral molecule P₄. The numerical values of the observed frequencies are in agreement with the theoretical expressions and yield $K_1 = 1.68 \times 10^8$ dynes/cm and $K_2 = 0.396 \times 10^{-11}$ dynes cm/radian for the primary valence and directed valence force constants respectively. On the assumption that this value of K_1 refers to a single bond, the oscillation frequency that is to be expected of P = P molecule is calculated as 742 and compared with the value 779 obtained from band spectra. The calculated specific heat at 9° C is 19.8 calories which is in good agreement with the experimental value, namely 22.0 calories.

DIFFRACTION OF LIGHT BY ULTRASONIC WAVES.

By K NAGABHUSHANA RAO

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(Communicated by Sir C V Raman, Kt, FRS, NL)

1 Introduction

A theory of the diffraction of light by high-frequency sound waves was developed by Sir C V Raman and Mr N S Nagendra Nath jointly, and later also by the latter independently, and was published in a series of papers in these *Proceedings* (These will be referred to below for brevity as R-N I, II, III, IV, V and N I) In a paper published in the *Physica*, July 1937 (referred to below as V C), Van Cittert has treated the case of normal incidence, starting from the usual expression for a pencil of light and considering the light fluctuations at successive points in the medium and thus also the diffraction effects, he obtains a system of differential equations, and solves them in a series of Bessel-functions of which the first term agrees with the simplified theory contained in R-N I In the present paper it will be shown that the results of the more general theory of Raman and Nath (R-N IV and N I) for the case of normal incidence are completely identical with those of Van Cittert The latter's method is then extended to the case of oblique incidence and the results thus obtained are proved to be also in agreement with those of Raman and Nath for this case contained in their papers (R-N V and N I) The solution is developed *in extenso*, as a series of Bessel-functions The method of parts as developed in Mr Nagendra Nath's recent paper for two systems of sound-waves is extended, and the resulting generalised difference-differential equation solved

NOTATION

μ_0' = Refractive index of the medium in the undisturbed state

μ = Maximum variation of the refractive index from μ_0'

λ = Wave-length of incident light

λ^* = Wave-length of sound wave

ν^* = Frequency of the sound wave

$$n = \mu(y, t) = \mu_0' - \mu \sin 2\pi \left(\nu^* t - \frac{y}{\lambda} \right)$$

= refractive index of the medium.

2 Normal and Oblique Incidence.

Considering the case of normal incidence, the results of R-N IV, and those of V C are proved to be the same as follows —

- (a) The restrictions under which the results are valid
- (b) The angles of inclination of the various orders of spectra to a fixed line
- (c) The expressions for the intensities, must be the same in both the theories

The incident light will be diffracted at angles given by $\sin \theta = \pm \frac{n\lambda}{\lambda^*}$ for the n th order (R-N IV), where θ is the angle with the x axis Van-Cittert's theory also gives the same expression ($\sin i_n = \frac{n\lambda}{\lambda^*}$ where i_n is the angle of the n th order with the axis of x)

The difference-differential equation as in V C is

$$\frac{dS_p}{d\xi} = -\frac{1}{\nu_0} \left(\frac{\mu_p}{\mu_0} - \mu_0 \right) S_p + \frac{1}{2} \{S_{p-1} - S_{p+1}\}, \quad (1)$$

where $\mu_p = \frac{2\pi\mu_0'}{\lambda} \cos r_p$, $\nu_p = \frac{2\pi\mu}{\lambda} \cos r_p$, and $\xi = \frac{2\pi\mu x}{\lambda}$

$-\left(\frac{\mu_p}{\nu_0} - \frac{\mu_0}{\mu}\right) = \frac{\mu_0'}{\mu} (1 - \cos r_p)$, and from the relation $\sin r_p = \frac{p\lambda}{n\lambda^*}$,

$$= \frac{1}{2} p^2 \frac{\lambda^2 \mu_0'}{\mu n^2 \lambda^{*2}} = \frac{1}{2} p^2 \frac{\lambda^2}{\mu \mu_0' \lambda^{*2}}$$

(neglecting powers of μ higher than the first)

$$= \frac{1}{2} p^2 \beta \text{ where } \beta = \frac{\lambda}{\mu \mu_0' \lambda^{*2}}.$$

∴ The equation takes the form

$$\frac{dS_p}{d\xi} = -\frac{1}{2} p^2 \beta S_p + \frac{1}{2} \{S_{p-1} - S_{p+1}\} \quad (2)$$

The solution of this equation is given as below (V C)

$$\left. \begin{aligned} S_0 &= J_0 - 2i\beta J_2 + 2\beta^2 J_4 + \dots \\ S_1 &= J_1 + i\beta J_3 - \beta^2 J_5 + \dots \\ S_2 &= J_2 + 5i\beta J_4 - 21\beta^2 J_6 + \dots \\ S_3 &= J_3 + 14i\beta J_5 + \dots \end{aligned} \right\} \text{where } J_n = J_n \left(\frac{2\pi\mu x}{\lambda} \right) \quad (2a)$$

Expressing these in powers of ξ , we have

$$\begin{aligned} S_0 &= 1 - \frac{\xi^2}{4} - \frac{\beta \xi^2}{24} + \frac{\xi^4}{64} \left(1 + \frac{\beta^2}{3}\right) - \dots \\ S_1 &= \frac{\xi}{2} \left\{1 + \frac{\beta \xi}{4} - \left(1 + \frac{\beta^2}{3}\right) \frac{\xi^2}{8} + \dots\right\} \\ S_2 &= \frac{\xi^2}{8} \left\{1 + \frac{5\beta \xi}{6} - \frac{1}{4} \left(\frac{7\beta^2}{4} + \frac{1}{3}\right) \xi^2 + \dots\right\} \\ S_3 &= \frac{\xi^3}{48} \left\{1 + \frac{7\beta \xi}{4} + \dots\right\} \end{aligned} \quad (2b)$$

Intensity = $|S_p|^2$ for the p th order

$$\begin{aligned} \text{R-N IV} \\ \text{and N I} \end{aligned} \left\{ \begin{aligned} \psi_0 &= 1 - \frac{\xi^2}{4} - \frac{\rho \xi^2}{24} + \frac{1}{64} \left(1 + \frac{\rho^2}{3}\right) \xi^4 + \dots \\ \psi_1 &= \frac{\xi}{2} \left\{1 + \frac{\rho \xi}{4} - \frac{1}{24} (\rho^2 + 3) \xi^2 - \frac{\rho}{192} (\rho^2 + 10) \xi^3 + \dots\right\} \\ \psi_2 &= \frac{\xi^2}{8} \left\{1 + \frac{5\rho \xi}{6} - \frac{1}{4} \left(\frac{7}{4} \rho^2 + \frac{1}{3}\right) \xi^2 + \dots\right\} \\ \psi_3 &= \frac{\xi^3}{48} \left\{1 + \frac{7\rho \xi}{4} + \dots\right\} \end{aligned} \right. \quad (2c)$$

Intensity of the p th order = $|\psi_p|^2$

$\rho = \frac{\lambda^2}{\mu\mu_0'\lambda'^2} = \beta$ and ξ signifies the same in both. Hence the expressions for the intensities are the same. The difference-differential equation is the same in both the cases

$$i.e., |\psi_p|^2 = |S_p|^2. \quad (3)$$

μ is small and of the order of 10^{-5} . β must be less than 1.

$$\beta = \frac{\lambda^2}{\mu\mu_0'\lambda'^2} = 0(10^{-1}) < 1 \quad \rho < 1 \quad \left\{ \begin{aligned} \lambda &= 0(10^{-5}) \\ \lambda' &= 0(10^{-5}) \\ \mu &= 0(10^{-5}) \\ \mu_0' &= 0(1) \end{aligned} \right.$$

Thus ρ also satisfies the condition

The results for the case of normal incidence from the general theory (R-N IV and N I) and of V C are thus the same

For the case of oblique incidence, we first have the same equation (1).

$$\frac{dS_p}{d\xi} = -\frac{i(\mu_p - \mu_0)}{\nu_0} S_p + \frac{1}{2} (S_{p-1} - S_{p+1}). \quad (3a)$$

The angles of emergence for the various orders are given by

$$\sin r_p \pm 1 - \sin r_p = \pm \frac{\lambda}{n\lambda^0} \quad (\text{V C})$$

$$\sin r_p - \sin r_{p-1} = \frac{\lambda}{n\lambda^0}$$

$$\sin r_{p-1} - \sin r_{p-2} = \frac{\lambda}{n\lambda^0}$$

$$\sin r_1 - \sin r_0 = \frac{\lambda}{n\lambda^0}$$

$$\therefore \sin r_p - \sin r_0 = p \cdot \frac{\lambda}{n\lambda^0}$$

Let the angle of incidence be ϕ ($i_0 = \phi$) We have the relation $\frac{\sin i_p}{\sin r_p} = n$
(refractive index of the medium)

$$\sin i_p = \sin \phi + p \frac{\lambda}{\lambda^0} \quad (3b)$$

This equation is the same as in R-N. II (oblique incidence)

$$-\left(\frac{\mu_p - \mu_0}{\nu_0}\right) = \frac{\mu_0'}{\mu} \left\{ \frac{\cos r_0 - \cos r_p}{\cos r_0} \right\}$$

$$\cos r_0 = \sqrt{1 - \frac{\sin^2 \phi}{n^2}} = 1 \text{ (neglecting powers of } \phi \text{ higher than the first)}$$

$$\cos r_p = \sqrt{1 - \left(\frac{\sin \phi}{n} + p \frac{\lambda}{n\lambda^0}\right)^2}$$

$$= 1 - \frac{1}{2} \left\{ \frac{p^2 \lambda^2}{n^2 \lambda^{02}} + 2p \frac{\sin \phi \lambda}{n^2 \lambda^{02}} \right\} \text{ (neglecting higher terms)}$$

$$\begin{aligned} -\left(\frac{\mu_p - \mu_0}{\nu_0}\right) &= \frac{\mu_0'}{2\mu} \left\{ p^2 \frac{\lambda^2}{n^2 \lambda^{02}} + 2p \frac{\lambda \sin \phi}{n^2 \lambda^{02}} \right\} \\ &= \frac{1}{2} \left\{ p^2 \frac{\lambda^2}{\mu \mu_0' \lambda^{02}} + 2p \frac{\lambda \sin \phi}{\mu \mu_0' \lambda^{02}} \right\} \end{aligned}$$

Setting $\beta = \frac{\lambda^2}{\mu \mu_0' \lambda^{02}}$ and $a = \frac{2\lambda \sin \phi}{\mu \mu_0' \lambda^{02}} = a\beta$ the equation becomes

$$2 \frac{dS_p}{d\xi} = \beta (p^2 + ap) + (S_{p-1} - S_{p+1}) \quad (4)$$

3 The Difference-Differential Equation

where $C_0 = i\beta ((p^2 + ap)$

$$a_{0,1} = 0$$

$$a_{00} = 0$$

$$a_{0, n+1} - a_{0, n-1} = -\{a_{1, n} - a_{-1, n}\}$$

$$a_{p, p+1} - a_{p-1, p} = C_p$$

$$a_{p+n+p+1} - a_{p-1+p+n} + a_{p+1+p+n} - a_{p+p+n-1} = C_p a_{p,p+n}$$

$$a_{p-1, p+n} - a_{p-2, p+n-1} + a_{p, p+n-1} - a_{p-1, p+n-2} = C_{p-1} a_{p-1, p+n-1}$$

$$a_{1, n+2} - a_{0, n+1} + a_{2, n+1} - a_{1, n} = C_1 a_{1, n+1}$$

On adding, we have

which can also be written as

$$a_{p, p+1} - a_{p-1, p} = C_p$$

$$a_{p, p+2} = \sum_p C_p a_{p, p+1}$$

$$= \sum_1^p C_p (C_1 + C_2 + \dots + C_p) = \frac{1}{2} \sum_{r=1}^p \sum_{s=1}^p C_r C_s,$$

$$= \frac{1}{2} \left\{ \left(\sum_1^p C_r \right)^2 + \sum_1^p C_r^2 \right\}.$$

$$a_{p, p+1} = \frac{1}{2} \left\{ \left(\sum_1^p C_r \right)^2 + \sum_1^p C_r^2 \right\} \quad (7a)$$

$$a_{p, p+1} = a_{0, 1} - \{C_1 + C_2 + \dots + C_{p+1}\} + \sum_1^p C_p a_{p, p+1}$$

$$a_{p, p+1} = - \left\{ C_{-1} + \sum_1^{p+1} C_r \right\} + \sum_1^p C_r C_r C_r \rightarrow (\text{all like terms being counted once only}) \quad (7b)$$

$$C_p = i\beta (p^2 + ap).$$

$$\left\{ \begin{aligned} a_{p, p+1} &= i\beta \left\{ \frac{p(p+1)(2p+1)}{6} + a \cdot \frac{p(p+1)}{2} \right\} \\ a_{p, p+1} &= - \frac{\beta^2}{2} \left\{ \frac{p(p+1)(2p+1)(10p^3 + 33p^2 + 23p - 6)}{180} \right. \\ &\quad \left. + \frac{a}{3} p^2 (p+1)^2 (p+2) + \frac{a^2}{12} p(p+1)(p+2)(3p+1) \right\} \\ a_{p, p+1} &= - i\beta \left\{ \frac{(p+1)(p+2)(2p+3)}{6} + 1 + \frac{a}{2} p(p+3) \right\} + \sum_1^p C_p a_{p, p+1} \end{aligned} \right\}$$

Expressions for the amplitudes S_0, S_1, \dots are as below

$$\begin{aligned} S_0 &= J_0 - 2i\beta J_1 + 2\beta^2 (1 + a^2) J_2 + 2i\beta \{5 + \beta^2 (1 + a^2)\} J_3 \\ &\quad - 2\beta^2 \{(27 + 9a^2) + \beta^2 (1 + 6a^2 + a^4)\} J_4 \\ &\quad - 2i\beta \{18 + \beta^2 (113 + 119a^2) + \beta^4 (1 + 10a^2 + 5a^4)\} J_5 \\ &\quad + 2\beta^2 \{(246 + 22a^2) + \beta^2 (459 + 922a^2 + 55a^4) + \beta^4 (1 + 15a^2 \\ &\quad + 15a^4 + a^6)\} J_6 + \end{aligned}$$

$$\begin{aligned} S_1 &= J_1 + i\beta (1 + a) J_2 - \beta^2 (1 + a^2) J_3 - i\beta \{(6 + 2a) + \beta^2 (1 + a^2)\} J_4 \\ &\quad + \beta^2 \{(28 + 30a + 10a^2) + \beta^2 (1 + a^4)\} J_5 + i\beta \{(25 + 3a) \\ &\quad + \beta^2 (114 + 196a + 122a^2 + 24a^4) + \beta^4 (1 + a^6)\} J_6 \\ &\quad - \beta^2 \{(273 + 190a + 31a^2) + \beta^2 (460 + 1044a + 928a^2 + 364a^4 \\ &\quad + 56a^6) + \beta^4 (1 + a^6)\} J_7 + \dots \end{aligned}$$

$$\begin{aligned} S_2 &= J_2 + i\beta (5 + 3a) J_3 - \beta^2 (21 + 24a + 7a^2) J_4 - i\beta \{(15 + 5a) \\ &\quad + \beta^2 (85 + 141a + 79a^2 + 15a^4)\} J_5 \\ &\quad + \beta^2 \{(214 + 176a + 38a^2) + \beta^2 (341 + 738a + 604a^2 + 222a^4 \\ &\quad + 31a^6)\} J_6 + i\beta \{(39 + 16a) + \beta^2 (2291 + 2849a + 1205a^2 \\ &\quad + 175a^4) + \beta^4 (1364 + 3634a + 3892a^2 + 2096a^4 + 568a^6 + 62a^8)\} J_7 + \dots \end{aligned}$$

$$S_3 = J_3 + i\beta (14 + 6a) J_4 - \beta^2 (147 + 120a + 25a^2) J_5 - i\beta \{(31 + 9a) + \beta^2 (1408 + 1662a + 664a^2 + 90a^3)\} J_6 \\ + \beta^2 \{(973 + 618a + 132a^2) + \beta^2 (13013 + 19910a + 11566a^2 + 3024a^3 + 270a^4)\} J_7 + \dots$$

$$S_4 = J_4 + i\beta (30 + 10a) J_5 - \beta^2 (627 + 400a + 65a^2) J_6 \\ - i\beta \{(56 + 14a) + \beta^2 (11440 + 10570a + 3304a^2 + 350a^3)\} J_7 \\ + \beta^2 \{(3872 + 2114a + 329a^2) + \beta^2 (653653 + 771990a + 344570a^2 + 68880a^3 + 3770a^4)\} J_8 + \dots$$

$$S_5 = J_5 + i\beta (55 + 15a) J_6 - \beta^2 (2002 + 1050a + 140a^2) J_7 \\ - i\beta \{(92 + 20a) + \beta^2 (61490 + 36830a + 12054a^2 + 1050a^3)\} J_8 \\ + \dots$$

$$S_6 = J_6 + i\beta (91 + 21a) J_7 - \beta^2 (5378 + 2402a + 266a^2) J_8 \\ - i\beta \{(141 + 21a) + \beta^2 (255098 + 155570a + 36042a^2 + 2646a^3)\} J_9 + \dots$$

$$S_7 = J_7 + i\beta \{(140 + 28a)\} J_8 - \beta^2 (12138 + 4704a + 462a^2) J_9 + \dots$$

$$S_p = J_p + i\beta \left\{ \frac{p(p+1)(2p+1)}{6} + \frac{a}{2} p(p+1) \right\} J_{p+1} \\ - \frac{\beta^2}{2} \left\{ \frac{p(p+1)(2p+1)(10p^3 + 33p^2 + 23p - 6)}{180} + \frac{a}{3} p^3(p+1)^2(p+2) \right. \\ \left. + \frac{a^2}{4} p(p+1)(p+2)(3p+1) \right\} J_{p+2} + \dots + a_{p,p+n} J_{p+n} + \dots$$

$$\text{where } J_n = J_n \left(\frac{2\pi\mu x}{\lambda} \right).$$

4 Systems of Parallel Sound Waves.

Let us consider the case of three systems of sound waves with different frequencies, amplitudes and wave-lengths. The refractive index of the medium is given by $\mu(y, t) = \mu_0 + \sum_{r=1}^3 \mu_r \sin 2\pi \left(\nu_r t - \frac{y}{\lambda_r} \right)$. It can easily be proved that combinational orders are present and that they occur at angles given by $\left(\sin \theta = r \frac{\lambda}{\lambda_1} + s \frac{\lambda}{\lambda_2} + t \frac{\lambda}{\lambda_3} \right)$ for the (r, s, t) th order. Extending the method of parts as in Mr Nath's recent paper, it can easily be seen that the equation giving the amplitudes of successive orders is

$$2 \frac{d}{dx} \phi_{r,s,t}(x) = \sigma_1 \{ \phi_{r-1,s,t} - \phi_{r+1,s,t} \} + \sigma_2 \{ \phi_{r,s-1,t} - \phi_{r,s+1,t} \} \\ + \sigma_3 \{ \phi_{r,s,t-1} - \phi_{r,s,t+1} \} \text{ where } \sigma_r = \frac{2\pi\mu_r}{\lambda}. \quad (8)$$

The boundary conditions are $\phi_{r,s,t}(0) = 0$, and $\phi_{0,0,0}(0) = 1$

This can easily be generalised to the case of N systems of sound waves

To solve the equation

$$2 \frac{d}{dz} \phi_{r,s,t}(z) = \sigma_1 \{ \phi_{r-1,s,t} - \phi_{r+1,s,t} \} + \sigma_2 \{ \phi_{r,s-1,t} - \phi_{r,s+1,t} \} \\ + \sigma_3 \{ \phi_{r,s,t-1} - \phi_{r,s,t+1} \} \quad (9)$$

with the conditions $\begin{cases} \phi_{r,s,t}(0) = 0 \\ \phi_{0,0,0}(0) = 1 \end{cases}$

Let $\phi_{r,s,t}(z) = \phi \frac{e^{\rho z}}{\xi_1^{r+1} \xi_2^{s+1} \xi_3^{t+1}}$. This is a solution of the above equation if $2\rho = \sum_{r=1}^3 \sigma_r \left(\xi_r - \frac{1}{\xi_r} \right)$. The most general solution is obtained by summing up similar solutions.

i.e.,

$$\phi_{r,s,t}(z) = \left(\frac{1}{2\pi i} \right)^3 \iiint \phi(\xi_1, \xi_2, \xi_3) e^{\frac{z}{2} \left\{ \sum_{r=1}^3 \sigma_r \left(\xi_r - \frac{1}{\xi_r} \right) \right\}} \frac{d\xi_1}{\xi_1^{r+1}} \frac{d\xi_2}{\xi_2^{s+1}} \frac{d\xi_3}{\xi_3^{t+1}} \quad (9a)$$

where ϕ is any function of ξ_1, ξ_2, ξ_3 . To obtain the solution satisfying the given boundary conditions, we can regard the quantities (ξ_r) as complex variables and take each integral round a closed contour which encircles the origin once

The boundary conditions are

$$\begin{cases} (1) \phi_{r,s,t}(0) = 0 & r \neq s, t \neq 0 \\ (2) \phi_{0,0,0}(0) = 1 \end{cases}$$

$$(1) \text{ gives } \left(\frac{1}{2\pi i} \right)^3 \oint \oint \oint \phi(\xi_1, \xi_2, \xi_3) \frac{d\xi_1}{\xi_1^{r+1}} \frac{d\xi_2}{\xi_2^{s+1}} \frac{d\xi_3}{\xi_3^{t+1}} = 0$$

This implies that $\phi(\xi_1, \xi_2, \xi_3)$ is a constant $= \alpha = 1$ by (2)

$$\therefore \phi_{r,s,t}(z) = \left(\frac{1}{2\pi i} \right)^3 \oint \oint \oint e^{\frac{z}{2} \left\{ \sum_{r=1}^3 \sigma_r \left(\xi_r - \frac{1}{\xi_r} \right) \right\}} \frac{d\xi_1}{\xi_1^{r+1}} \frac{d\xi_2}{\xi_2^{s+1}} \frac{d\xi_3}{\xi_3^{t+1}}$$

We know that $\frac{1}{2\pi i} \oint \frac{e^{\frac{\sigma z}{2} \left(t - \frac{1}{t} \right)}}{\xi^{n+1}} d\xi = J_n(\sigma z)$. This can be proved as

follows

$$\oint \frac{1}{2\pi i} e^{\frac{z}{2} \left(t - \frac{1}{t} \right)} \frac{d\xi}{\xi^{n+1}} = \text{Residue at the origin}$$

$$e^{\frac{z}{2} \xi} e^{-\frac{z}{2\xi}} = \sum_0^{\infty} \frac{\left(\frac{z}{2} \xi \right)^n}{\underline{n}} \cdot \sum_0^{\infty} \frac{\left(-\frac{z}{2\xi} \right)^n}{\underline{n}}$$

Coefficient of ξ^n is given by

$$\begin{aligned} & \left(\frac{z}{2} \right)^n \frac{1}{\underline{n}} - \left(\frac{z}{2} \right)^{n+2} \frac{1}{\underline{1} \underline{n+1}} + \left(\frac{z}{2} \right)^{n+4} \frac{1}{\underline{2} \underline{n+2}} \\ &= \left(\frac{z}{2} \right)^n \left\{ \frac{1}{\underline{n}} - \frac{\left(\frac{z}{2} \right)^2}{\underline{1} \underline{n+1}} + \dots \right\} \\ &= \left(\frac{z}{2} \right)^n \left\{ \sum_0^{\infty} (-1)^r \left(\frac{z}{2} \right)^{2r} \frac{1}{\underline{r} \underline{n+1}} \right\} \\ &= J_n(z) \end{aligned}$$

$$\frac{1}{2\pi i} \oint e^{\frac{z}{2} \left(t - \frac{1}{t} \right)} \frac{d\xi}{\xi^{n+1}} = J_n(z)$$

$$\begin{aligned} \phi_{r,s,t}(z) &= \frac{1}{2\pi i} \oint e^{\frac{\sigma_1 z}{2} \left(t_1 - \frac{1}{t_1} \right)} \frac{d\xi_1}{\xi_1^{r+1}} \cdot \frac{1}{2\pi i} \oint e^{\frac{\sigma_2 z}{2} \left(t_2 - \frac{1}{t_2} \right)} \frac{d\xi_2}{\xi_2^{s+1}} \times \\ &\quad \times \frac{1}{2\pi i} \oint e^{\frac{\sigma_3 z}{2} \left(t_3 - \frac{1}{t_3} \right)} \frac{d\xi_3}{\xi_3^{t+1}} \end{aligned}$$

$$\boxed{\phi_{r,s,t}(z) = J_r(\sigma_1 z) J_s(\sigma_2 z) J_t(\sigma_3 z)} \quad (10)$$

The generalised form of the above equation can be written as

$$\begin{aligned} 2 \frac{d}{dz} \phi_{n_1, n_2, \dots, n_N}(z) &= \sigma_1 \left\{ \phi_{n_1-1, n_2, \dots, n_N} - \phi_{n_1+1, n_2, \dots, n_N} \right\} \\ &+ \sigma_2 \left\{ \phi_{n_1, n_2-1, \dots, n_N} - \phi_{n_1, n_2+1, \dots, n_N} \right\} + \dots \\ &+ \sigma_N \left\{ \phi_{n_1, n_2, \dots, n_{N-1}} - \phi_{n_1, n_2, \dots, n_{N+1}} \right\}. \end{aligned} \quad (11)$$

where n_1, n_2, \dots, n_N are integers and $\{\sigma_r\}$ are constants $\left(\sigma_r = \frac{2\pi\mu_r}{\lambda} \right)$.

Proceeding as before, we have the general solution given by

$$\phi_{n_1, n_2, \dots, n_N}(z) = \left(\frac{1}{2\pi i}\right)^N \underbrace{\iint \dots \iint_N}_{\text{over } \xi_1, \xi_2, \dots, \xi_N} \phi(\xi_1, \xi_2, \dots, \xi_N) e^{\frac{z}{2} \left\{ \sum_{r=1}^N \sigma_r \left(t_r - \frac{1}{t_r} \right) \right\}} \\ \times \frac{d\xi_1}{\xi_1^{n_1+1}} \frac{d\xi_2}{\xi_2^{n_2+1}} \dots \frac{d\xi_N}{\xi_N^{n_N+1}} \quad (11a)$$

To obtain the solution satisfying the boundary conditions

$$\left. \begin{aligned} \phi_{n_1, n_2, \dots, n_N}(0) &= 0 \\ \phi_{0,0,\dots,0}(0) &= 1 \end{aligned} \right\}$$

we regard the quantities (ξ_r) as complex variables and integrate them round contours enclosing the origin once. We therefore get,

$$\phi_{n_1, n_2, \dots, n_N}(z) = \left(\frac{1}{2\pi i}\right)^N \underbrace{\oint \dots \oint_N}_{\text{over } \xi_1, \xi_2, \dots, \xi_N} \phi(\xi_1, \xi_2, \dots, \xi_N) e^{\frac{z}{2} \left\{ \sum_{r=1}^N \sigma_r \left(t_r - \frac{1}{t_r} \right) \right\}} \\ \frac{d\xi_1}{\xi_1^{n_1+1}} \frac{d\xi_2}{\xi_2^{n_2+1}} \dots \frac{d\xi_N}{\xi_N^{n_N+1}} \\ = \prod_{r=1}^N \left\{ \frac{1}{2\pi i} \oint e^{\frac{\sigma_r z}{2} \left(t_r - \frac{1}{t_r} \right)} \frac{d\xi_r}{\xi_r^{n_r+1}} \right\} \\ = J_{n_1}(\sigma_1 z) \cdot J_{n_2}(\sigma_2 z) \dots J_{n_N}(\sigma_N z)$$

$$\boxed{\phi_{n_1, n_2, \dots, n_N}(z) = \prod_{r=1}^N J_{n_r}(\sigma_r z)} \quad (12)$$

$$\text{Intensity} = |\phi_{n_1, n_2, \dots, n_N}(z)|^2 = \prod_{r=1}^N J_{n_r}^2(\sigma_r z) \quad (13)$$

This same expression has been obtained by E. Fues by applying the simplified theory of Raman-Nath (R-N I). In conclusion it is my greatest pleasure to record my respectful thanks to Professor Sir C. V. Raman, for suggesting the present investigation and for much valuable guidance and criticism in the course of the work.

5 Summary

The results of Raman and Nath in their general theory of the diffraction light by ultrasonic waves at normal and oblique incidences are shown to be in complete agreement with those of Van Cittert for the case of normal incidence and also with those obtained by extending Van Cittert's method to the case of oblique incidence. The amplitude function for the latter case is developed *in extenso* in a series of Bessel functions. The expression for the

intensity with normal incidence in the case of N systems of sound waves is $|J_{n_1}(\sigma_1 z) J_{n_2}(\sigma_2 z) \cdots J_{n_N}(\sigma_N z)|^2$, where n_1, n_2, \cdots, n_N are the orders excited. This result is the same as that which has been obtained by E. Fues by applying the simplified Raman-Nath method to the case considered

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ON LINEAR TRANSFORMATIONS OF BOUNDED SEQUENCES—III.

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PART III

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§ 13 General Remarks

THIS part deals with a subclass of T [T as defined in 2.1 of Part I of this paper] We designate the direct and inverse transformations of this class by U and U^{-1} , and prove that these transformations, and others defined by their products are commutative We further shew that transformations corresponding to differences of any real order form a subclass of the group defined by U , U^{-1} , and their products In (16) we shew that some important theorems of Anderson (A.1)* are, either deducible from, or particular cases of, theorems of Parts I and II of this paper In (17) we discuss the generalization of Knopp's results on "Mehrfach monotone folgen" (K.2)†

§ 14 A Class of Commutative Transformations

Let $\|a_m n\|$ define a U Then besides the four conditions of (2.1) of Part I, condition (e), namely, $a_{n,n+p} = a_p$ for all n , i.e., $a_{0p} = a_{1,p+1} = \dots = a_{n,n+p} = \dots$, characterizes a_{mn} , so that a_{mn} for U is characterized as follows:

$$(a') a_{n,n} = 1 \quad (b') a_{mn} = 0, n < m \quad (c') a_p < 0 \text{ for all } p > 1 \quad [14.1]$$

$$(d') -\sum_{p=1}^{\infty} a_p \leq 1 \quad \text{We see that a } U \text{ is defined completely by a sequence } \{a_p\} \text{ satisfying (c') and (d')}$$

(A.1)*. A. F. Anderson *Studier over Cesaro's summabilitets methode* (Danish) See the second chapter entitled "Om differencer".

(K.2)†. K. Knopp, "Mehrfach Monotone folgen," *Mathematische Zeitschrift*, 1925, 22, 75-85

In section 2 of Part I we established the existence of a unique reciprocal matrix $\|\beta_{m,n}\|$ such that $\|\beta_{m,n}\| \cdot \|a_{m,n}\| = \|\delta_{m,n}\|$ (unit matrix). Since any U is a T it follows that in this case also $\|\beta_{m,n}\|$ the reciprocal matrix exists.

Further from section 2 of Part I, we obtain

$$\beta_{n,n+p} = - \sum_{k=1}^p a_{n,n+k} \beta_{n+k,n+p} \quad (2.6)$$

We can at once deduce $\beta_{n,n+p} = b_p$ for all n , and

$$b_p = - \sum_{k=1}^p a_k b_{p-k} \quad [14.2]$$

We obtain the following results also easily $b_0 = 1$, $b_n > 0$, and from (14.2) it follows that b_n is given by the equation

$$\left(\sum_0^{\infty} b_n x^n \right) \left(1 + \sum_{n=1}^{\infty} a_n x^n \right) = 1 \quad [14.3]$$

If U_1 and U_2 are defined by $\{a_n^1\}$ and $\{a_n^2\}$, it is easy to prove

(1) $U_1 U_2 = U_2 U_1$, (2) if $\|c_{m,n}\|$ defines $U_1 U_2$ then $c_{n,n+p} = a_p^3$ for all n , (3) a_p^3 is given by the equation

$$1 + \sum_{p=1}^{\infty} a_p^3 x^p = \left(1 + \sum_1^{\infty} a_p^1 x^p \right) \left(1 + \sum_1^{\infty} a_p^2 x^p \right) \quad [14.4]$$

The matrix of any product of U 's and U^{-1} 's is always characterized by condition (e) of 14.1. If $\{\bar{a}_p\}$ defines the product \bar{a}_p can be calculated in all cases from an equation of the type of (14.4). It is quite easy to shew that the commutative property is true for any product of U 's and U^{-1} 's

§ 15 Differences of any Real Order

THEOREM Transformations defined by differences of any real order form a subclass of the class formed by U 's, U^{-1} 's, and their products.

Lemma 1 If $0 < \gamma < 1$ then we shall prove that $\Delta^\gamma = U(\gamma)$

$$\begin{aligned} \text{Formally the difference } \Delta^\gamma v_n &= v_n - \gamma v_{n+1} + \frac{\gamma(\gamma-1)}{[2]} v_{n+2} \\ &\quad - \frac{\gamma(\gamma-1)(\gamma-2)}{[3]} v_{n+3} + \dots \\ &= v_n - \gamma v_{n+1} - \frac{\gamma(1-\gamma)}{[2]} v_{n+2} - \dots \\ &\quad - \frac{\gamma(1-\gamma) \dots (p-1-\gamma)}{[p]} v_{n+p} - \dots \end{aligned}$$

Consider a transformation $U(\gamma)$ defined by $\{a_n\}$ as follows

$$a_1 = -\gamma, a_2 = -\frac{\gamma(1-\gamma)}{[2]}, \dots, a_p = -\frac{\gamma(1-\gamma)(p-1-\gamma)}{[p]}$$

then, $a_p < 0$ for $p > 1$ and $-\sum_1^{\infty} a_p = 1$.

Hence conditions (c') and (d') of (14.1) are fulfilled and we have

$$\Delta^\gamma = U(\gamma) \quad [15.1]$$

Lemma 2 If $0 < \gamma < 1$ $\Delta^{-\gamma} = \{U(\gamma)^{-1}\}$ [15.2]

By (14.3) this is obvious

Proof of Theorem Let $U(1) = \Delta^1$ as in (15.1)

$$\text{Let } [U(1)]^{-1} = \Delta^{-1} \text{ as in (15.2)}$$

Then if Δ^p be a difference of any positive order, consider the transformation

$$S = [U(1)]^m U(\gamma)$$

where

$$m = [p] \text{ and } \gamma = (p)$$

and

$$U(\gamma) = \Delta^\gamma$$

If $\{a_p\}$ defines S , it is given as in (14.4) by

$$\begin{aligned} 1 + \sum a_p x^p &= (1-x)^m \left(1 - \gamma x - \gamma \binom{1-\gamma}{2} x^2 \dots \right) \\ &= (1-x)^{m+\gamma} = (1-x)^p \end{aligned}$$

so that

$$a_n = (-1)^n \frac{p(p-1)\dots(p-n+1)}{[n]}$$

i.e.,

$$S = \Delta^p = [U(1)]^m U(\gamma) \quad [15.3]$$

If p is negative we prove in exactly the same way as above

$$\Delta^p = \{[U(1)]^{-1}\}^m \cdot \{U(\gamma)\}^{-1}$$

where

$$m = (-p) \text{ and } \gamma = (-p) \quad [15.4]$$

Hence the theorem

§ 16 Deductions of Some Theorems of Anderson

We propose in this section to derive Soetning 3, 4, and 5 of Anderson on differences from theorems of Part I and II of this paper

Soetning III (page 20 of Anderson's Book A.1)

$$(a) \text{ If } x_n = O(1) \quad r > 0 \quad s > -1 \quad \text{and } r+s > 0$$

then

$$\Delta^s \{ \Delta^r(x_n) \} = \Delta^{r+s}(x_n)$$

$$(b) \text{ If } x_n = O(1) \quad r > 0 \quad s > -1 \quad \text{and } r+s > 0$$

then

$$\Delta^s \{ \Delta^r(x_n) \} = \Delta^{r+s}(x_n)$$

Proof of (a) Leaving aside the trivial case of $s > 0$ we shall shew that (a) is a particular case of Theorem XVIII of section 11§, Part II of this paper

Let $s < 0$ and $s = -q$ $q < 1$ choose q_1 such that $q < q_1 < 1$ and $q_1 < r$ so that $r = q_1 + t$, $t > 0$

Then by Theorem of 15§

$$\Delta^t = U_{p_1} \cdot U_{p_2} \cdots U_{p_h}$$

and

$$\Delta^r = U(q_1) \cdot U_{p_1} \cdots U_{p_h}$$

where

$$U(q_1) = \Delta^{q_1} \quad \text{as in (15.1)}$$

and

$$\Delta^s = [U(q)]^{-1}$$

Since $\{x_n\}$ is bounded by Theorem II of Part I so is $(U_{\rho_1} U_{\rho_2} \dots U_{\rho_k})(x_n) = y_n$

We shall now shew that $[U(q)]^{-1} \cdot [U(q_1)(y_n)] = \{[U(q)]^{-1} \cdot U(q_1)\}(y_n)$

Let $\|\beta_{mn}\|$ define $[U(q_1)]^{-1}$ and $\|s_{mn}\|$ define $[U(q)]^{-1}$

$$\text{then } s_{n, n+p} = s_p = \frac{q(q+1)(q+p-1)}{p} = O(p^{q-1})$$

$$\text{and } \beta_{n, n+p} = b_p = \frac{q_1(q_1+1)(q_1+p-1)}{p} = O(p^{q_1-1})$$

$$\text{therefore } \frac{s_{n, n+p}}{\beta_{n, n+p}} = O(p^{q-q_1}) \quad \frac{s_{n, n+p}}{\beta_{n, n+p}} \rightarrow 0 \quad \text{as } p \rightarrow \infty$$

Obviously s_p is bounded and y_n bounded. Hence the three conditions of Theorem XVIII are fulfilled and we have

$$\begin{aligned} [U(q)]^{-1} \cdot [U(q_1)(y_n)] &= \{[U(q)]^{-1} \cdot U(q_1)\}(y_n) = \Delta^{q_1-q} y_n \\ &= U(q_1 - q)(y_n) \end{aligned}$$

But $y_n = U_{\rho_1} \dots U_{\rho_k}(x_n)$

and by Theorem II of Part I

$$\begin{aligned} [U(q_1 - q)] [U_{\rho_1} U_{\rho_2} \dots U_{\rho_k}(x_n)] &= [U(q_1 - q) U_{\rho_1} \dots U_{\rho_k}](x_n) \\ &= \Delta^{r+s}(x_n) \end{aligned}$$

Proof of (b) Leaving aside the trivial case of $s > 0$, this is a particular case of Theorem X of section 8§, Part II (refer 8.32)

Let $s = -q \quad q > 0 \quad r = q + t \quad t \geq 0$

$$\begin{aligned} \text{then } \Delta^s &= [U(q)]^{-1} \quad \text{and} \quad \Delta^r = \Delta^q \cdot \Delta^t \\ &= U(q) \cdot U_{\rho_1} U_{\rho_2} \dots U_{\rho_k} \end{aligned}$$

Since x_n is a null sequence by 8.32 of Part II

$$[U(q)]^{-1} [U(q) U_{\rho_1} U_{\rho_2} \dots U_{\rho_k}(x_n)] = U_{\rho_1} U_{\rho_2} \dots U_{\rho_k}(x_n)$$

or

$$\Delta^s [\Delta^r(x_n)] = \Delta^{r+s}(x_n)$$

Statement Soetning IV and V of Anderson —

Soetning IV (a)—If $x_n = O\left(\frac{1}{n^a}\right)$, $a > 0$, $r > -a$, $s > -1-a$, $r+s > -a$

$$\text{then } \Delta^s [\Delta^r(x_n)] = \Delta^{r+s}(x_n)$$

Soetning IV (b)—If $x_n = O\left(\frac{1}{n^a}\right)$, $a > 0$, $r > -a$, $s > -1-a$, $r+s > -a$

$$\text{then } \Delta^s [\Delta^r(x_n)] = \Delta^{r+s}(x_n)$$

Soetning V (c)—If $x_n = O\left(\frac{1}{n^a}\right)$, $a > 0$, $r > -a$, $s > -1-a$, $r+s > -a$

$$\Delta^s [\Delta^r(x_n)] = \Delta^{r+s}(x_n) \quad \text{when the latter exists}$$

We shall shew that these are particular cases of Theorems VI, VII, VIII and IX of Part II of this paper. There is a considerable amount of overlapping of the various cases occurring in (a), (b), (c). In any particular case of (a) we shall have

$$(a') \quad s \geq 1 - a_2, \quad r \geq -a_2, \quad \text{and} \quad r + s \geq -a_2, \quad \text{where} \quad 0 < a_2 < a$$

The cases of (b) which do not occur under (a) are

$$(b') \quad s = -1 - a, \quad r > -a, \quad r + s > -a$$

The cases of (c) which do not occur under (a) and (b) are

$$(c') \quad r + s = -a, \quad r > -a, \quad s \geq -1 - a$$

We propose to further divide (a'), (b') and (c') as follows

$$(a') \quad - (a_1') \text{ when } s \geq -a_2, \quad (a_2') \quad s = -a_2 - q \quad 0 \leq q \leq 1$$

$$(b') \quad - \text{only one case } (b_1')$$

$$(c') \quad - (c_1') \text{ when } r \text{ and } s \text{ are negative}$$

$$i.e., \quad r = -a_2, \quad s = -a_2, \quad a_2 > 0, \quad a_2 > 0 \quad \text{and} \quad a_2 + a_2 = a$$

$$(c_2') \text{ when } 0 \leq r \leq 1 \quad \text{and} \quad s = -a - r$$

We shall shew that (a₁') is a particular case of Theorem VII of Part II

(a₂'), (b₁') and (c₂') are particular cases of Theorem IX of Part II

and (c₁') is a particular case of Theorem VI of Part II

Proof (a₁') $r \geq -a_2, \quad s \geq -a_2 \quad \text{and} \quad r + s \geq -a_2$

By 15.4 $\Delta^{-a} = U_1^{-1} \cdot U_2^{-1} \cdot U_k^{-1}$ and the most general way of taking Δ^r and Δ^s would be $\Delta^r = (U_1^{-1} \cdot U_2^{-1} \cdot U_l^{-1} U_{p_1} \cdot U_{p_2} \cdot U_{p_r})$ and $\Delta^s = (U_{q_1} U_{q_2} \cdot U_{q_s} \cdot U_{l+1}^{-1} \cdot U_{l+2}^{-1} \cdot U_k^{-1})$

If $\|\beta_{n, n+p}\|$ defines $(U_1^{-1} \cdot U_k^{-1})$ then $\beta_{n, n+p} = b_p =$

$$\frac{a_2(a_2 + 1) \cdots (a_2 + p - 1)}{p!} = O(p^{a_2-1})$$

and
$$\sum_{p=0}^n b_p = B_n = O(n^{a_2})$$

Let $a_2(1 + \delta) = a, \quad \text{since } a_2 < a, \quad \delta > 0,$

By hypothesis
$$x_n = O\left(\frac{1}{n^a}\right) = O\left(\frac{1}{B_n^{1+\delta}}\right)$$

Hence by (8.20) of Theorem VII of Part II

$$\begin{aligned} \Delta^s[\Delta^r(x_n)] &= (U_{q_1} U_{q_2} \cdot U_{q_s} \cdot U_{l+1}^{-1} \cdots U_k^{-1}) [(U_1^{-1} \cdot U_l^{-1} U_{p_1} \cdots U_{p_r}(x_n)] \\ &= (U_{q_1} \cdots U_{q_r} \cdot U_{l+1}^{-1} \cdots U_k^{-1} \cdot U_1^{-1} \cdot U_l^{-1} U_{p_1} \cdots U_{p_r})(x_n) = \Delta^{r+s}(x_n) \end{aligned}$$

Proof of (a₂') $s = -a_2 - q \quad 0 \leq q \leq 1 \quad r = q + t \quad t > 0$

since
$$x_n = O\left(\frac{1}{n^a}\right) \text{ as above } x_n = O\left(\frac{1}{B_n^{1+\delta}}\right) = O\left(\frac{1}{B_n}\right).$$

$$\begin{aligned} \text{Let} \quad \Delta^{-a} &= U_1^{-1} \cdot U_k^{-1} \\ \Delta^r &= U(q) \\ \text{then} \quad \Delta^s &= (U_1^{-1} \cdot U_k^{-1}) [U(q)]^{-1} \\ \Delta^r &= U(q) U_{\rho_1} U_{\rho_2} \cdot U_{\rho_r} \end{aligned}$$

If $\|\beta_{n, n+\rho}\|$ defines $(U_1^{-1} \cdot U_k^{-1})$ and $b_\rho = \beta_{n, n+\rho}$ and $B_n = \sum_{\rho > 0}^n b_\rho$

since by hypothesis $x_n = 0 \left(\frac{1}{B_n} \right)$ we have by (8.30) and (8.31) of Theorem IX of Part II

$$\begin{aligned} \Delta^s [\Delta^r(x_n)] &= [U_1^{-1} \cdot U_k^{-1} \{U(q)\}^{-1}] (U(q) U_{\rho_1} U_{\rho_2} \cdot U_{\rho_r})(x_n) \\ &= (U_1^{-1} \cdot U_k^{-1} \cdot U_{\rho_1} U_{\rho_2} \cdot U_{\rho_r})(x_n) \\ &= \Delta^{r+s}(x_n) \text{ when the latter exists} \end{aligned}$$

But the latter exists by Theorem VII since $x_n = 0 \left(\frac{1}{B_n^{1+\delta}} \right)$, $\delta > 0$

Hence (a'_2) is established

Proof of (b') $s = -1 - a$ $r = 1 + t$ $t > 0$ $x_n = 0 \left(\frac{1}{n^a} \right)$

Let $\Delta^1 = U(1)$, $\Delta^{-a} = (U_1^{-1} \cdot U_k^{-1})$

then if $\|\beta_{nn}\|$ defines $(U_1^{-1} \cdot U_k^{-1})$ $\beta_{nn+\rho} = b_\rho$

$$= \frac{a(a+1)(a+p-1)}{p} = 0 \quad (p^{a-1})$$

$$\text{and } B_n = \sum_{\rho=0}^n b_\rho = 0 \quad (n^a)$$

We therefore have $\Delta^r = U(1) \cdot U_{\rho_1} U_{\rho_2} \cdot U_{\rho_r}$

$$\Delta^s = [U(1)]^{-1} U_1^{-1} U_k^{-1}$$

and since $x_n = 0 \left(\frac{1}{B_n} \right)$

$$\begin{aligned} \Delta^s [\Delta^r(x_n)] &= \{[U(1)]^{-1} U_1^{-1} \cdot U_k^{-1}\} [U(1) \cdot U_{\rho_1} \cdot \cdot U_{\rho_r}] \\ &= (U_1^{-1} \cdot U_k^{-1} \cdot U_{\rho_1} \cdot \cdot U_{\rho_r})(x_n) = \Delta^{r+s}(x_n) \text{ if the latter exists by} \\ &\text{(8.30) and (8.31) of Theorem IX of Part II} \end{aligned}$$

But the latter exists since $x_n = 0 \left(\frac{1}{n^a} \right)$ and $r+s > -a$ by Theorem VII

Proof of (c') In this case argument is identical with that of (b') except in the last step where it must be noted that the equality will be valid if $\Delta^{-a} x_n$ exists

Proof of (c') $r = -a_2$ $s = -a_1$ $a_2 + a_1 = a$ $a_2 > 0$ $a_1 > 0$ $x_n = 0 \left(\frac{1}{n^a} \right)$

Let $\|\beta_{n,p}\|$ define Δ^{-a_1} . We shall prove that

$$\left| \sum_{p=A}^{\infty} \beta_{n,p} |x_p| \right| = O\left(\frac{1}{A^{a_1}}\right)$$

Proof $\beta_{n,n+p} = b_p = O(p^{a_1-1})$ and $\sum b_p = B_n = O(n^{a_1})$

and $x_n = \frac{\epsilon(n)}{n^a} = \frac{\epsilon(n)}{n^{a_1(1+\delta)}} = \frac{\epsilon(n)}{B_n^{1+\delta}}$ where $\epsilon(n) \rightarrow 0$ as $n \rightarrow \infty$

Hence by result (1) of Theorem VII

$$\left| \sum_{p=A}^{\infty} \beta_{n,p} |x_p| \right| \leq \frac{\epsilon^1(A)}{B_A^\delta} = \frac{\epsilon^1(A)}{A^{a_1}} = O\left(\frac{1}{A^{a_1}}\right).$$

If $\|\beta'_{n,p}\|$ defines Δ^{-a_1} then $\beta'_{n,n+p} = b'_p = O(p^{a_1-1})$

$$\text{and } \sum b'_p = B'_n = O(n^{a_1})$$

Hence $\left| \sum_A^{\infty} \beta_{n,p} |x_p| \right| = O\left(\frac{1}{B_A}\right)$ uniformly for all n

Hence the conditions of Theorem VI are fulfilled and we have by the same theorem

$$\Delta^{-a_1} [\Delta^{-a_1} (x_n)] = \Delta^{-a} (x_n) \text{ when the latter exists}$$

§ 17 Generalization of some Theorems of Knopp

His results in the paper (K 1) are as follows

Given $x_n > 0$ and $x_n = 0$ (1) then

I If $\Delta^a (x_n) > 0$ for all n , then $\Delta^\beta (x_n) \geq 0$ for $0 \leq \beta \leq a$ (Satze 6 of his paper)

II If $a \geq 1$ and $0 < \beta < a-1$ and $x_n > 0$ $x_n = 0$ (1) and $\Delta^a (x_n) > 0$ for all n

then $\Delta^\beta (x_n) = O\left(\frac{1}{n^\beta}\right)$ [Satze 9 of his paper]

and two particular cases of II are also given as Satze 7 and Satze 8 of his paper

It will be shewn that,

$$\text{if } a > 0 \quad (x_n) = y_n \quad y_n > 0$$

then for all $0 \leq \beta < a \quad \Delta^\beta (y_n) = \Delta^{-(a-\beta)} (y_n)$ [17.1]

and in particular $x_n = \Delta^{-a} y_n$ is an immediate consequence of Theorem IV of Part I

In particular $x_0 = \Delta^{-a} y_0 = \sum A_n^{a-1} \Delta^a (x_n) = \sum A_n^{a-1} |\Delta^a (x_n)|$
Hence the conditions of Hjaelpsoetning III B of Anderson on page 34 of his book (A.1) are satisfied and result II of Knopp follows at once as a particular

case of the theorem of Anderson It is rather remarkable that Knopp has not noticed this We will here give generalizations of results I and II applicable to U 's

THEOREM I Let $S = U_1 U_2 U_3 \cdots U_k$ and $S(x_n) = y_n$
 and $S' = U_{r+1} U_{r+2} \cdots U_k$ and $S'(x_n) = z_n$
 If $x_n = 0$ (1) and $y_n > 0$ for all n ,
 then $S'(x_n) = (U_1^{-1} U_2^{-1} \cdots U_r^{-1})(y_n)$
 and $S'(x_n) > 0$ for all n [17.2]
Proof $y_n = S(x_n) = (U_1 U_2 U_r)(U_{r+1} \cdots U_k)(x_n)$
 $= (U_1 U_2 U_r)\{S'(x_n)\}$ by Theorem II of Part I
 $= (U_1 U_2 U_r)(z_n)$

Also since $x_n = 0$ (1) so is $z_n = 0$ (1) by Theorem II of Part I

Hence by repeated application of Theorem IV of Part I just as in the corollary to it

$$z_n = (U_r)^{-1} (U_{r-1})^{-1} \cdots (U_1)^{-1} (y_n) \\
= \sum \beta_{r,n+n+\rho_1} \sum \beta_{r-1,n+\rho_1,n+\rho_2} \cdots \sum \beta'_{n+\rho_{r-1},n+\rho} y_{n+\rho} \quad [17.3]$$

where $\|\beta'_{m,n}\|$ defines $(U_r)^{-1}$ The multiple series on the right can be summed up in any manner since $\beta_{m,n} \geq 0$ and $y_n \geq 0$

$$z_n = (\sum \beta_{r,n+n+\rho_1} \beta_{r-1,n+\rho_1,n+\rho_2} \cdots \beta'_{n+\rho_{r-1},n+\rho}) y_{n+\rho} \\
= \sum_{\rho=0}^{\infty} \bar{\beta}_{n+\rho} y_{n+\rho}$$

where $\|\beta_{m,n}\| = \|\beta'_{m,n}\| \cdot \|\beta_{r-1,m,n}\| \cdots \|\beta'_{m,n}\|$

Hence $z_n = (U_1^{-1} U_2^{-1} \cdots U_r^{-1})(y_n) = (U_{r+1} \cdots U_k)(x_n)$

since $y_n > 0$ and all $\beta_{m,n} \geq 0$ we have $z_n > 0$

and in particular we have $x_n = (U_1^{-1} U_k^{-1})(y_n)$, when $r = k$ [17.4]

When the U 's are Δ 's we have as a deduction from above the result of (17.1) namely —If $\Delta^a(x_n) = y_n > 0$ for all n $a > 0$

then $\Delta^\beta(x_n) = \Delta^{-(a-\beta)} y_n$

and in particular $x_n = \Delta^{-a} y_n$

THEOREM II Let $U(1) = \Delta^1$ and $S = [U(1) \cdot U_1 U_2 U_3 U_k]$

Let $\|\bar{\beta}_{m,n}\|$ define $U_1^{-1} U_2^{-1} \cdots U_k^{-1}$ $S' = U_1 U_2 \cdots U_k$

Now $\beta_{m,n+\rho} = b_\rho$ Let $\sum_0^n b_\rho = B_n$

then if

$x_n = 0$ (1) and $S(x_n) = y_n > 0$ for all n , then $S'(x_n) = 0 \left(\frac{1}{B_n}\right)$. [17.5]

$$\begin{aligned}
 \text{Proof} \quad \text{By 17.4 } x_n &= \{[U(1)]^{-1} U_1^{-1} \cdot U_2^{-1} \quad U_k^{-1}\} (y_n) \\
 &= \{U(1)\}^{-1} (U_1^{-1} \quad U_k^{-1}) (y_n) \\
 &= U(1)^{-1} \cdot (\Sigma \beta_{n+n+p} y_{n+p}) \\
 &= U(1)^{-1} \left(\sum_0^{\infty} b_p \cdot y_{n+p} \right) \\
 &= \sum_0^{\infty} B_p y_{n+p}
 \end{aligned}$$

$$\text{and} \quad x_0 = \sum_0^{\infty} B_p y_p$$

$$\text{and} \quad S'(x_n) = [U(1)]^{-1} (y_n) = \sum_n^{\infty} y_p$$

$$\text{Now} \quad \sum_n^{\infty} y_p = \sum_n^{\infty} \frac{B_p y_p}{B_p} \leq \frac{1}{B_p} \Sigma B_p y_p = 0 \left(\frac{1}{B_n} \right)$$

since $\Sigma B_p y_p$ converges and $B_0 \leq B_1 \leq \dots \leq B_n \leq$

$$\text{Hence} \quad S'(x_n) = 0 \left(\frac{1}{B_n} \right) \quad \text{Thus proving (17.5)}$$

Result II of Knopp follows immediately from this

$$\text{for} \quad \text{let } U(1) = \Delta^1 \quad U_1 U_2 U_k = \Delta^a \quad a > 0$$

$$\text{If} \quad \Delta^{1+a}(x_n) > 0 \text{ for all } n$$

$$\text{then} \quad \Delta^a x_n = 0 \left(\frac{1}{n^a} \right)$$

for B_n in this case $= O(n^a)$

Knopp's Satze 7 is an immediate consequence of this. His Satze 8 takes the following interesting form in terms of U 's

If $U(x_n) = y_n$ be > 0 for all n , $x_n > 0$ and $x_n = 0(1)$ and $\sum_0^{\infty} x_n$ convergent, then,

$B_n x_n \rightarrow 0$ as $n \rightarrow \infty$ where $\{b_n\}$ defines U^{-1} as in (14.3) and

$$B_n = \sum_{p=0}^n b_p \quad \text{Putting } r_n = x_n + x_{n+1} + \dots$$

$$\text{we have} \quad \Delta r_n = x_n = U(1)(r_n)$$

$$\text{Hence} \quad [U(1) U](r_n) = y_n > 0 \quad \text{for all } n$$

$$\text{Hence} \quad U(r_n) = 0 \left(\frac{1}{B_n} \right) \text{ by (17.5)}$$

$$\text{But } U(r_n) = \sum_n^{\infty} x_p + a_1 \sum_{n+1}^{\infty} x_p + a_2 \sum_{n+2}^{\infty} x_p + \dots, \text{ where } \{a_n\} \text{ defines } U$$

The right-hand side is an absolutely convergent double series since

$$\sum_1^{\infty} |a_n| = - \sum_1^{\infty} a_n \leq 1 \text{ and } \sum x_n \text{ is convergent}$$

Hence $U(r_n) = x_n + x_{n+1}(1 + a_1) + x_{n+2}(1 + a_1 + a_2) + \dots$

since $1 + a_1 + a_2 + a_n > 0$ by condition (d') of 14.1

we have $x_n < U(r_n)$

$$\text{Hence } x_n = O\left(\frac{1}{B_n}\right). \quad [17 \ 6]$$

Erratum.

Vol VIII, No 1, page 55, line 31

Instead of "These interactions are the 'exchange effects' "
read "These interactions are not the 'exchange effects' "

COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE ORGANIC AND INORGANIC SALTS OF ISONITROSO-DIPHENYL-THIO- BARBITURIC ACID AND ITS HIGHER HOMOLOGUES AND ANALOGUES.

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ISONITROSO-MALONYL-UREA or violuric acid, which forms interesting coloured salts with alkali hydroxides and organic bases, has been exhaustively examined by Ghatak and Dutt,¹ who found that the stronger the basic character of the base, the greater is the intensity of the colour of the salt that is formed in combination with violuric acid. They examined the absorption spectra of the organic salts of violuric acid along with their dissociation constants and came to the conclusion that there is a general relationship between the two values although no hard and fast mathematical relationships could be derived from them. Previous workers in this field, namely, Hartley,² Hantzsch,³ Meek and Watson⁴ had only confined their attention to the absorption spectra of free violuric acid and the sodium and potassium salts in water. They had already taken notice of the fact that in dry non-hydroxylic solvents, violuric acid was quite colourless, but in hydroxylic solvents, as well as in wet non-hydroxylic solvents, it had a distinct pink coloration.

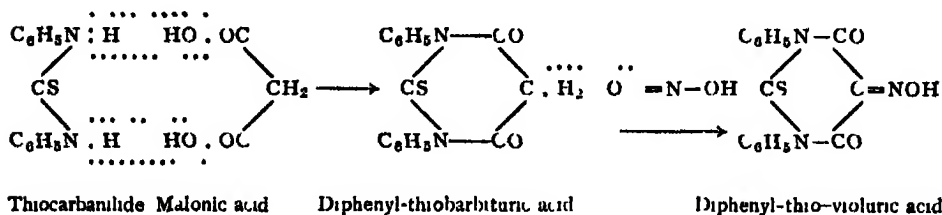
Later on Gaund and Dutt⁵ took up the study of violantin and alloxantin and their organic salts and found that the intensity of their coloration was even greater than the corresponding compounds of violuric acid. Both the compounds are monobasic in nature and form well-defined salts very similar to those of violuric acid, with the difference that unlike the latter, the former undergo hydrolytic decomposition in water. Consequently, the dissociation constants could not be determined and the absorption spectra were found in alcoholic solution.

The next interesting work in this connection was done by Lal and Dutt,⁶ who took up the study of isonitroso-thio-barbituric acid or thio-violuric acid,

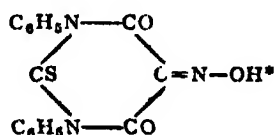
which was prepared by them for the first time by the action of nitrous acid on thio-barbituric acid. The alkali and organic salts of this compound were found to be highly coloured substances, yielding fluorescent and intensely purple solutions with absorption bands between 5900–6025 Å. They were in this respect far more coloured than the corresponding salts of violuric acid, and it appeared highly interesting to note the tremendous difference in colour and absorption brought about by the introduction of an atom of sulphur in the molecule of violuric acid in place of an atom of oxygen. The effect of sulphur on the colour of organic compounds and dyestuffs has previously been noticed by former workers, *e.g.*, by Purvis, Jones and Tasker,⁷ who noticed that the thio-oxalates of alkalies are yellow in colour, whereas the corresponding oxalates are colourless, by Dutt and Watson,⁸ who have shown that many mercaptan derivatives of azo-dyes and thio-fluorescein are deeper in colour than the corresponding dyes containing oxygen in place of sulphur, by Reid and his collaborators⁹ who also worked in similar lines to Dutt and Watson, and by Dey and Dutt,¹⁰ who worked on dyestuffs prepared from thio-diglycollic acid. But in none of these works mentioned above was the intensity of colour found to be so much enhanced by the introduction of an atom of sulphur in place of an atom of oxygen, as in the case of compounds derived from thio-violuric acid. Lal and Dutt examined the absorption spectra of these compounds and also the dissociation constants of a number of them which were soluble in water, but on comparing the results thus obtained, they came to the conclusion that the colour of thio-violurates is not intimately connected with electrolytic dissociation, and in fact intense colours were possessed by compounds which were altogether insoluble in water or hydroxylic solvents, and whose absorption spectra had to be determined in acetone or chloroform solutions.

On account of the interesting results obtained with thio-violuric acid, it was naturally expected that any further loading of the molecule of the substance with heavy substituents might result in the production of a compound capable of yielding salts with even greater intensity of colour than that obtained from thio-violuric acid. This expectation from the theoretical point of view has now been realised in the case of 1,3-diphenyl-thio-violuric acid. It is the aim of the present investigation to examine the effect of loading on the molecule of thio-violuric acid by the introduction of two phenyl or even heavier groups, and also to compare their salts with the corresponding salts of diphenyl-violuric acid, which would differ from the former only in possessing an atom of sulphur in place of the oxygen atom.

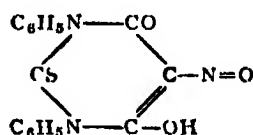
1 3-Diphenyl-thio-violuric acid has now been prepared for the first time by the action of nitrous acid on 1 3-diphenyl-thio-barbituric acid, which in its turn has been obtained by the condensation of thiocarbamide with malonic acid in presence of acetyl-chloride



Isonitroso-diphenyl-thio-barbituric acid or diphenyl-thio-violuric acid is a monobasic acid and may be represented by formula (1) shown below, in which the hydrogen atom marked with an asterisk is replaceable by metal. This is the *oximino-ketonic* form



(1) Oximino-ketonic form



(2) Nitroso enolic form

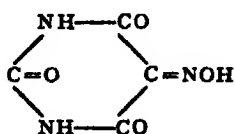
But an alternative structure can be formed due to the tautomerism of the marked hydrogen atom to give the *nitroso-enolic formula* (2), which is equally capable of existence. This contains the highly strained grouping $\text{N}=\text{O}$, and hence according to the "Theory of colour on the basis of molecular strain" advanced by Dutt,¹¹ it must be a highly coloured substance. On the other hand if the oximino-ketonic formula be correct, then diphenyl-thio-violuric acid should not have any colour at all, or at best only a pale yellow colour. We find that the compound in question is an orange coloured solid dissolving in solvents like acetone to an orange solution. It appears that in solution as well in the solid state, the substance exists mainly in the oximino-ketonic form. But this state of affairs becomes considerably modified when a salt formation of the acid occurs by treatment with alkali or an organic base. Under such circumstances, on account of the greater load of the substituting metal or basic radical, the tautomerism between the two above-mentioned forms will be far more difficult and the more highly strained configuration (2) will result as soon as its existence becomes possible due to the following reasons. The $-\text{CO}$ -groups in the molecule of diphenyl-thio-violuric acid are really the residues of carboxyl groups, and they still retain the acidic character

in a modified form due to the presence of the NPh-groups in the vicinity, whose basic character they have more than neutralised. When such a group enolises by the transference of a hydrogen atom, it becomes more acidic than a -NOH group (*cf* uric acid and the ureides with the oximes of aldehydes and ketones). It can be easily seen therefore that in order to neutralise an alkali like sodium hydroxide or an organic base, the original weakly acidic oximino-ketonic form has to tautomerise into the more acidic nitroso-enolic form in order that a neutral salt formation may take place. And once the tautomeric hydrogen atom becomes substituted in the latter form, the nitroso-enolic structure becomes fixed due to salt formation, and on account of the heavy load cannot tautomerise back into the oximino-ketonic form. It is due to this that a highly strained but stable structure results, which is in fact responsible for the intense colour of the diphenyl-thio-violurates.

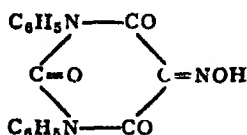
As a further proof of the above theoretical exposition of the colour phenomenon of the salts of diphenyl-thio-violuric acid, it may be pointed out that weak bases like aniline, picoline, quinoline, *iso*quinoline, etc., form molecular combinations with the acid in dry acetone solution which are only slightly coloured, *i.e.*, which are either yellow or orange. But in the presence of only a trace of water, true salt formation takes place immediately with production of the usual intense blue or green colorations. It is therefore quite evident that the real basic character of the base has to be developed in the presence of a minimum quantity of water before the true nitroso-enolic structure of diphenyl-thio-violuric acid with its concomitant highly acidic nature can be formed with a view to real salt formation. In other words, it is a question of ionisation of the base before the salt formation may take place. Very weak bases like β -naphthylamine, *m*-xylidene, etc., do not produce any salts for the same reason.

The effect of sulphur on colour as seen on comparison of the absorption spectra of salts of diphenyl-thio-violuric acid with the corresponding salts of diphenyl-violuric acid (Prakash and Dutt,¹⁸ work just published) is also very interesting. Whereas the characteristic colour of the latter is purple-violet with the absorption maxima in the vicinity of 5900 Å, the characteristic colour of the former is bluish-green to deep emerald-green, with absorption maxima in the neighbourhood of 6500 Å in many cases. Besides this there is another aspect of the "Theory of colour on the basis of molecular strain" advanced by Dutt (*loc cit*), namely, "In a system that is under strain, the effect of load will be to increase the strain, provided it acts within close proximity of the strain, the further away the load is from the centre of the

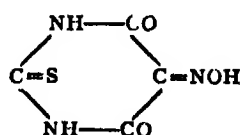
strain, the less will be the effect" exemplified, when we compare the four types of compounds given below —



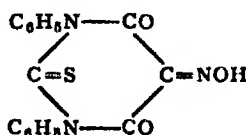
(3) Violuric acid Pink salts,
Abs Max. 5305 Å



(4) Diphenyl violuric acid Violet
salts, Abs Max 5900 Å



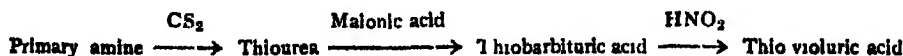
(5) Thio-violuric acid Violet
salts, Abs Max 5900 Å.



(6) Diphenyl thio violuric acid.
Green salts, Abs. Max. 6500 Å

We find that a load of 16 units is as effective in deepening the colour of violuric acid to thio-violuric acid, as a load of 154 units to the same substance under slightly different conditions, with formation of diphenyl-violuric acid. The reason is obvious on scrutiny, since we find that in the former case the load has been applied at the centre of the strain itself, i.e., at the double bond. But in the latter case we find that the phenyl groups are one bond removed from the double bond, and are consequently less effective as loads in deepening the colour. Similar phenomenon will be observed when (3), (4) and (6) are compared together.

On account of the great success achieved with the preparation of diphenyl-thio-violuric acid and its organic and inorganic salts and, also the fulfilment of the expectations as calculated from the theoretical point of view with regard to this compound, attempts were made to prepare other derivatives of thio-violuric acid containing heavier substituents than the two phenyl groups. With this object in view, the following scheme was worked out with an equally great success.



The following primary aromatic amines were successfully used in this connection: *o*-toluidine, *m*-toluidine, *p*-toluidine, *m*-xylydine, *o*-anisidine, *p*-phenetidine and α -naphthylamine, and the corresponding substituted thio-violuric acids obtained. All these higher homologues and analogues of diphenyl-thio-violuric acids with the exception of the α -naphthyl

compound yield more intensely coloured compounds with alkalis and organic bases than the corresponding ones obtained from diphenyl-thio-violic acid, and their absorption bands are also higher up in the spectrum. This has been exactly according to expectations from the point of view of theoretical considerations. But in the case of the α -naphthyl compound, although the impure stuff yielded a green coloration with alkalis and organic bases, yet on purification and crystallisation, the substance was resolved into a compound giving only violet salts with them. Apparently this is the only anomaly in connection with the consideration of the large number of substances that have been examined in this investigation.

Experimental

Preparation of diphenyl-thio-barbituric acid—A mixture of thiocarbamide (20 gm), malonic acid (12 gm) and acetyl-chloride (18 cc) was heated on the water-bath under reflux for about 30 minutes. The mixture first became a completely homogeneous fluid which ultimately solidified to a compact light yellow crystalline mass. The product was broken up, ground fine with water in a mortar, filtered, washed, dried and crystallised from glacial acetic acid in bright yellow prismatic needles melting at 245°C .

The acid is sparingly soluble in most of the ordinary organic solvents in the cold, fairly soluble in boiling alcohol and hot glacial acetic acid, almost insoluble in chloroform, benzene and ether and insoluble in water. It dissolves easily in dilute caustic alkalis and ammonia.

Preparation of isonitroso-diphenyl-thio-barbituric acid or diphenyl-thio-violic acid—Diphenyl-thio-barbituric acid (20 gm) was dissolved in dilute sodium hydroxide (5 per cent) and a solution of sodium nitrite (20 gm) in the minimum quantity of water added. The mixture was filtered through thick cotton cloth, cooled with the addition of lumps of clear ice, and gradually acidified with the addition of ice-cold dilute sulphuric acid. The light buff coloured precipitate of the isonitroso compound was allowed to stand overnight, then filtered, washed with water, dried and crystallised from boiling glacial acetic acid, when it was obtained in the form of glistening orange rhombic prisms (see Plates IV and V) melting at 227°C .

Diphenyl-thio-violic acid is absolutely insoluble in water, but dissolves in boiling glacial acetic acid to the extent of only about 3 per cent and on cooling, practically the whole amount crystallises out. It is very slightly soluble in other neutral organic solvents, with the exception of acetone, in which it is fairly easily soluble, forming a bright orange non-fluorescent solution. On the addition of alkalis or organic bases, intense blue or green

colours are developed and in the majority of cases, the salt is precipitated in a crystalline and exceedingly beautiful form. The colour change is so sharp and rapid that diphenyl-thio-violuric acid can be used as an excellent indicator. The salts give absorption bands reaching much further into the red region than those given by the corresponding salts of thio-violuric acid. With the exception of the alkali salts, the rest are quite insoluble in water, but in acetone they are very easily soluble giving intense colorations which are augmented by the addition of a few drops of water and in this aqueous acetone medium, all the absorption spectra have been determined. All the salts of diphenyl-thio-violuric acid possess beautiful crystalline structure, are fairly stable, but melt with decomposition. The lowest decomposition temperature that has been recorded is in the vicinity of 130°C . Some of the alkaloid salts are rather unstable and become sticky and swell up due to decomposition, on keeping. Consequently they have to be prepared immediately before the examination of their properties. They all possess cubical crystalline structure. Contrary to expectation, they were found to be optically inactive, thus proving that racemisation took place along with salt formation. All the salts described in this paper have been prepared by mixing together equimolecular proportions of the acid and the base in acetone solution. In 90 per cent of the cases, the salt crystallised out completely but, in the rest, it had to be obtained by evaporation of the mother liquor.

Preparation of the higher homologues and analogues of diphenyl-thio-violuric acid was done in a similar way to the above. For the sake of abbreviation, the properties of the barbituric and violuric acids (Table I), the salts of diphenyl-thio-violuric acid (Table II) and some of the salts of the higher homologues and analogues of diphenyl-thio-violuric acid (Table III) are given in tabular forms at the end of the paper. Microphotographs of the crystalline structures of diphenyl-thio-violuric acid and its higher homologues and analogues have also been appended showing the exceedingly fine crystalline nature of these substances.

Summary and Conclusions

1 *Isomitoso*-diphenyl-thio-barbituric acid has been obtained for the first time by the action of nitrous acid on 1,3-diphenyl-thio-barbituric acid prepared in its turn by the action of diphenyl-thiourea on malonic acid in presence of acetyl chloride.

2 *Isonitroso*-diphenyl-thio-barbituric acid or diphenyl-thio-violuric acid has an orange colour in the solid state or in solution in organic solvents,

but on treatment with alkalis or organic bases, intense blue and green coloured salts are formed, the transition of colour being sufficiently strong and sharp for the substance to act as an excellent indicator

3 The change of colour from orange to blue or green has been shown from theoretical considerations to be due to a fundamental change in the constitution of the molecule from an oximino-ketonic to a nitroso-enolic structure

4 The above change in the molecular structure results in the production of a true nitroso-group, which from the point of view of a "Theory of colour on the basis of molecular strain" advanced by one of the present authors, has been shown to be the most highly strained amongst the chromophoric groups, and consequently produces the greatest intensity of colour

5 The loading effect of the two phenyl groups as well as that of the sulphur atom from the point of view of colour production has been discussed, and it has been shown that the effect is quite in accordance with the theory of colour advanced by Dutt

6 From the study of the absorption spectra of the salts of diphenyl-thio-violuric acid it has been found that their intensity of colour is roughly proportional to the strength of the basic character of the base entering into salt formation

7 Further study of the absorption spectra of the salts of a series of newly synthesised higher homologues and analogues of diphenyl-thio-violuric acid indicates that the effect of additional load on the molecule of the substance is to produce still further intensification of colour as expected from theoretical considerations, the greatest effect being produced by substituents in *meta*-positions closely followed by those in the *para*

TABLE I.
Properties of the Main Barbituric and Violuric Acids

Name (T B =thio-barbituric T V,=thio violuric acids)	Colour of solid	Remarks	Colour in solution (aqueous acetone)	M P	Absorption Maxima A	Analysis (% S Theo- retical with- in bracket)
<i>1 The barbituric acids</i>						
Diphenyl-T B	Pale yellow	Prisms	Yellow	245°	4650	10.62 (10.81)
Di-o-tolyl T B	Yellow	Rectangular prisms	Yellow	190°	4650	9.67 (9.87)
Di-m-tolyl T B	Light yellow	Fine needles	Yellow	265°	4550	9.52 (9.87)
Di-p-tolyl T B	Bright yellow	Rectangular prisms	Yellow	233°	4650	9.58 (9.87)
Di-m-xylyl T B	Yellow	Do	Yellow	247°	4720	9.50 (9.09)
Di-o-anisyl T B	Yellow	Fine needles	Yellow (deep)	248°	4720	8.35 (8.98)
Di-p-phenetyl T B	Light salmon pink	Do	Deep yellow	167°	4720	8.75 (8.33)
Di-α-naphthyl-T B	Greenish yellow	Cubical crystals	Orange yellow	216°	4960	8.52 (8.08)
<i>2 The Violuric Acids</i>						
Diphenyl T V	Orange red	Glistening hexa- gonal plates & prisms	Orange	227°	5130	9.95 (9.84)
Do (No 2)	Dull orange	Rectangular prisms & needles	Orange- yellow	220°	5050	9.30 (9.84)
Di-o-tolyl-T V	Buff	Rectangular plates	Yellow	200°	4755	9.04 (9.06)
Di-m-tolyl T V	Dull orange	Rhombic plates	Orange	216°	5160	9.21 (9.06)
Di-p-tolyl T V	Deep salmon- pink	Hexagonal plates	Reddish orange	128°	5180	9.02 (9.06)
Di-m-xylyl-T.V	Buff	Needles	Orange- yellow	165°	5060	8.85 (8.42)
Di-o-anisyl T V	Deep mahogany- brown	Glistening cubes	Orange red	212°	5220	7.81 (8.31)
Di-p-phenetyl-T.V.	Orange buff	Spindle-shaped prisms	Do	128°	5200	7.16 (7.74)
Di-α-naphthyl-T.V	Violet-black	Glistening roundish poly- gonal crystals	Brownish yellow	216°	5140	7.96 (7.52)

TABLE II
Properties of Diphenyl-thio-violurates

Name of the compound (D T =diphenyl thio violurate)	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M P (D)	Absorption Maxima λ	Analysis (% S Theoretical with in bracket)
Methylamine D T	Deep olive green	Glistening hexagonal prisms	Greenish blue	128°	6010	8.72 (8.98)
Dimethylamine D T	Brilliant green	Glistening hexagonal plates	Bluish emerald green	185°	6030	8.43 (8.64)
Trimethylamine D T	Olive green	Glistening prisms	Bluish green	123°	6015	8.30 (8.33)
Ethylamine D T	Deep olive green	Glistening needles	Deep olive green	176°	6050	8.52 (8.64)
Diethylamine D T	Brilliant green	Glistening hexagonal plates	Deep greenish blue	128°	6070	8.00 (8.04)
Allylamine D T	Greenish grey	Glistening prismatic needles	Bluish green	169°	6025	8.12 (8.37)
Isobutylamine D T	Deep green	Do	Indigo blue	178°	6000	8.53 (8.04)
Isoamylamine D T	Steel grey	Do	Deep blue	162°	6015	8.20 (7.76)
Quinoline D T	Salmon pink	Fine needles	Pale bluish green	176°	5920	7.32 (7.04)
Piperidine D T	Dull terra cotta	Do	Deep green	184°	6140	7.36 (7.80)
Isoquinoline D T	Salmon pink	Do	Grass green	174°	6009	7.37 (7.04)
Collidine D T	Light mauve	Do	Do.	186°	6010	7.57 (7.17)
Pyridine D T	Bluish green	Microscopic prisms	Yellowish green	178°	5980	7.52 (7.92)
α Picoline D T	Dull terra cotta	Prismatic needles	Sea green	188°	5940	7.31 (7.65)
Lepidine D T	Light bluish green	Fine needles	Turquoise blue	186°	6030	7.30 (8.83)
<i>o</i> Toluidine D T	Granite grey	Prismatic needles	Dirty brownish green	180°	6025	7.95 (7.40)
Quinaldine D T	Salmon pink	Fine needles	Bluish green	159°	6040	7.2 (6.83)
Phenetidine D T (p)	Chocolate brown	Prismatic needles	Dark olive green	136°	6020	6.73 (6.92)
Anisidine D T (o)	Greenish grey	Rhombic prisms	Do	128°	6000	7.64 (7.14)

TABLE II—(Contd)

Name of the compound (D T =diphenyl thio violurate)	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M P (D)	Absorption Maxima μ	Analysis (% S Theo- retical with in bracket)
α Naphthylamine D T	Dirty brown	Glistening prismatic needles	Dirty brownish green	161°	5860	6.92 (6.83)
p-Toluidine D T	Reddish brown	Prismatic needles	Grass green	199°	6030	8.10 (7.40)
m Toluidine D T	Light oak brown	Glistening hexa- gonal prisms	Greenish brown	164°	6020	7.78 (7.40)
Brucine D T	Bright bluish green	Cubical crystals	Azure-blue	180°	6050	4.83 (4.45)
Potassium D T	Deep emerald- green	Glistening rect- angular prisms	Brilliant green	219°	6560	8.84 (8.81)
Sodium D T	Greenish black	Do	Intense emerald green	128°	6610	9.39 (9.22)
Ammonium D T	Bluish grey	Rectangular prisms	Greenish blue	213°	6060	9.83 (9.35)
Quinine D T	Light bluish grey	Cubical crystals	Violet blue	139°	5950	5.51 (4.90)
Veratrine D T	Light greenish grey	Do	Moss-green	166°	6080	4.10 (3.49)
Cinchonidine-D T.	Greyish blue	Do	Deep violet	140°	5970	5.32 (5.16)
Morphine D T	Violet black	Do	Carmine red	93°	5780	5.67 (5.24)
Thebain D T	Dark grey	Do	Brownish red	123°	5825	4.83 (5.03)
Narcotin D T	Greenish grey	Do	Reddish brown	103°	5865	4.67 (4.33)

TABLE III

Salts of Higher Homologues and Analogues of Diphenyl-thio-voluric Acid.

Name of the compound	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M P (D)	Absorption Maxima λ	Analysis (% S Theo retical with in bracket)
(A) Acid Di o tolyl thio voluric Acid						
Methylamine salt	Dark olive green	Short hexagonal prisms	Deep olive green	153°	6060	8.21 (8.33)
Diethylamine "	Bright bluish-green	Rhombic plates	Greenish-blue	181°	6190	7.84 (7.51)
Triethylamine "	Violet grey	Small prismatic needles	Deep sage green	155°	6400	7.32 (7.76)
Quinoline "	Light buff	Fine needles	Olive green	212°	6075	7.11 (6.63)
Sodium "			Greenish blue		6190	
(B) Acid Di p tolyl thio voluric Acid						
Methylamine salt	Light grey	Very fine needles	Brilliant blue green	176°	6205	8.28 (8.33)
Diethylamine "	Bright bluish green	Fine prismatic needles	Brilliant green	142°	6420	7.45 (7.52)
Trimethylamine "	Light dull blue	Fine needles	Do	164°	6425	7.18 (7.76)
Sodium "			Greenish-blue		6150	
(C) Acid Di m tolyl thio voluric Acid						
Methylamine salt	Light greenish blue	Rectangular prisms	Dark olive green	160°	6315 (6220)	8.21 (8.33)
Diethylamine "	Brilliant green	Glistening cubes	Deep indigo blue	185°	6300 (6160)	7.84 (7.51)
Trimethylamine "	Greyish-blue	Do	Deep violet	107°	5850	7.32 (7.76)
Quinoline "	Light buff	Fine needles	Light dirty green	177°	6005	6.97 (6.63)
Sodium "			Bluish-green		6235	

TABLE III—(Contd.)

Name of the compound	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M P (D)	Absorption Maxima Å	Analysis (% S Theoretical with in bracket)
(D) Acid Di-m-xylyl-thio violuric Acid						
Methylamine salt	Brownish violet	Glistening rectangular prisms	Yellowish green	148°	6035	7.35 (7.76)
Diethylamine ..	Deep ash grey	Cubic crystals	Bright green	104°	6165	7.52 (7.04)
Trimethylamine ..	Dark violet-brown	Rectangular prisms	Greenish blue	138°	6150	7.61 (7.27)
Sodium ..			Brilliant green		6280	
(E) Acid Di-o-anisyl-thio violuric acid						
Methylamine salt ..	Medium grey	Rectangular prisms	Brilliant blue green	151°	6170	7.54 (7.45)
Diethylamine ..	Grey blue	Rhombic prisms	Emerald green	154°	6265	7.38 (6.98)
Trimethylamine ..	Violet-black	Rectangular prisms	Deep emerald green	105°	6280	7.36 (7.20)
Sodium ..			Green		6150	
(F) Acid Di-p-phenetyl-thio violuric acid						
Methylamine salt ..	Medium grey	Prismatic needles	Bluish emerald green	142°	6150	7.58 (7.20)
Diethylamine ..	Greenish grey	Cubical crystals	Emerald green	136°	6350	6.43 (6.58)
Trimethylamine ..	Greyish green	Rectangular plates	Deep emerald green	114°	6410	6.32 (6.77)
Sodium ..			Bluish green		6220	
Quinoline ..	Leather-brown	Rhombic plates	Brown red	136°	5980	6.41 (6.90)
(G) Acid Di-α-naphthyl-thio violuric acid						
Methylamine salt ..	Dark brown	Rectangular plates	Brownish red	147°	5990	7.42 (7.01)
Diethylamine ..	Black	Prismatic needles	Do	153°	5900	6.31 (6.42)
Trimethylamine ..	Black	Glistening prismatic needles	Do	112°	5860	7.04 (6.61)
Sodium ..			Violet		5900	

TABLE IV

Comparison of the Absorption Maxima of the Violurates, Thio-violurates and Diphenyl-thio-violurates

Absorption Maxima

Figures indicate wave-lengths in Angstrom units

Salt of	With Violuric acid	With Thio violuric acid	With Diphenyl thio violuric acid
Sodium	5830	5828	6610
Potassium	5830	5847	6560
Ammonium	5832	5837	6060
Methylamine	5782	5892	6010
Dimethylamine	5793	5858	6030
Trimethylamine	5712	5820	6015
Ethylamine	5697	5870	6050
Diethylamine	5699	5931	6070
Butylamine	5632	5850	6000
<i>o</i> Toluidine	5626	5928	6025
<i>m</i> Toluidine	5678	5941	6020
<i>p</i> Toluidine	5684	5950	6030
α -naphthylamine	5499	5597	5980
Pyridine	5692	5886	5980
α picoline	5692	5907	5940
Piperidine	5697	6023	6140
Quinoline	5683	5861	5920
Quinine	5537	5905	5950
Cinchonidine .	5557	5927	5970
Brucine .	5697	5975	6050

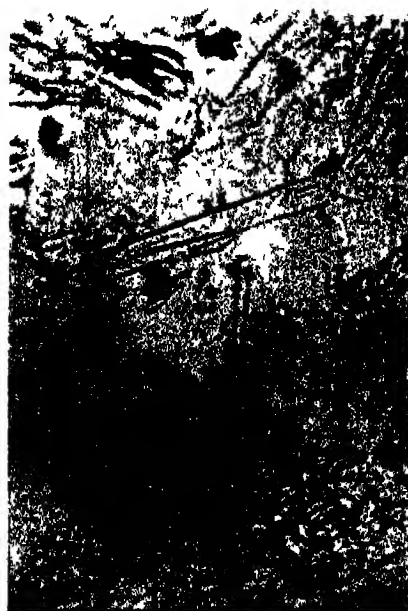
MICROPHOTOGRAPHS OF DIPHENYL-THIO-VIOURIC ACID AND ITS
HIGHER HOMOLOGUES AND ANALOGUES



Di-*p*-tolyl-thio-viouric acid



Diphenyl-thio-viouric acid



Di-*o*-tolyl-thio-viouric acid



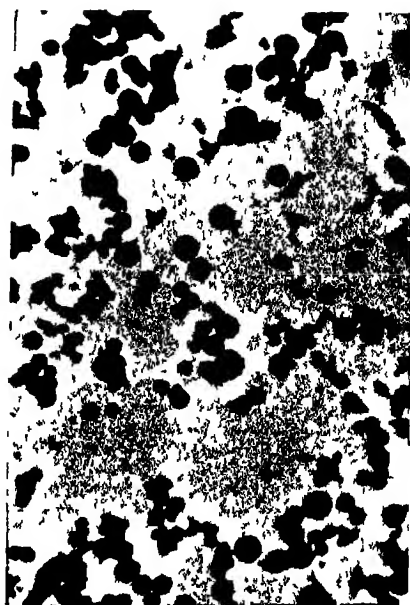
Di-*m*-tolyl-thio-viouric acid

(Miss) Ione Nitravati
Dharam Dass and
Sikhibhushan Dutt

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Di-o-anisyl-thio-violic acid



Di-α-naphthyl-thio-violic acid



Di-m-xyl-thio-violic acid



Di-p-phenetyl-thio-violic acid

TABLE V

Comparison of the Absorption Maxima of the Salts of Diphenyl-thio-violuric Acid and its higher Homologues and Analogues

Figures indicate wave lengths in Angstrom units

Acid (T V =thio violuric acid)	Methylamine salt	Diethylamine salt	Trimethyl amine salt	Quinoline salt	Sodium salt
Diphenyl T V	6010	6070	6015	5920	6610
D ₁ o tolyl T V	6060	6190	6400	6075	6190
D ₁ p tolyl T V	6205	6420	6425		6150
D ₁ m tolyl T V	6315	6300	5850	6005	6235
D ₁ m xylyl T V	[6035	6165	6150		6280
D ₁ o anisyl T V	6170	6265	6280		6150
D ₁ p phenetyl T V	6150	[6350	6410	5980	6220
D ₁ α naphthylamine T V	5960	5900	5860		5900

N B—*Meta* and *para* tolyl groups have the greatest effect on the colour of diphenyl thio-violurates

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A THEOREM IN THE ADDITIVE THEORY OF NUMBERS.

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In this paper I prove the

Theorem Let* ξ_1, ξ_2, ξ_3 be a set of increasing positive integers such that the number of ξ 's not exceeding x is greater than $c_1 x$ (for $x > x_0$) where c_1 is an absolute positive constant Then the number of solutions of

$$n = a\xi_u^2 + b\xi_v^2 + c\xi_w^2$$

where a, b, c are fixed positive integers and $n \leq x$, is greater than $c_2 x$ for large x where c_2 is an absolute positive constant

A case of this theorem is that the set of numbers which can be expressed in the form $ax^2 + by^2 + cz^2$ has positive density I do not know whether this result is a consequence of the theory of ternary quadratic forms

The proof of this theorem depends on the result that

$$\sum_{m \leq x} r^2(m) = O(x^2)$$

where $r(m)$ is the number of ways in which $m = ax^2 + by^2 + cz^2$ (x, y, z take +ve, -ve and 0 values and a, b, c are fixed positive integers)

The proof of the asymptotic relation, namely, that

$$\sum_{m \leq x} r^2(m) \sim Ax^2$$

where A is an absolute positive constant, will be developed in a future paper.

Notation We take the Farey series of order \sqrt{n} and $\xi_{p,q}$ denotes the segment for which

$$2\pi \left(\frac{p + p''}{q + q''} - \frac{p}{q} \right) \text{ and } 2\pi \left(\frac{p + p'}{q + q'} - \frac{p}{q} \right)$$

are the limits of variation of θ where $\frac{p''}{q''}$ and $\frac{p'}{q'}$ are the left-hand and right-hand neighbours respectively of $\frac{p}{q}$ in the Farey series of order \sqrt{n} .

* i.e., the ξ 's have "positive density" with respect to the natural numbers.

$$g(w) = \sum_{n=-\infty}^{\infty} w^{n^2} \quad (|w| < 1)$$

where $w = e^{\frac{2\pi i p/q - \frac{1}{n} + i\theta}{}}$

Then
$$f(w) = g(w^a) g(w^b) g(w^c) \\ = \sum_{m=0}^{\infty} r(m) w^m$$

where $r(m)$ is the function defined above

$$S = S_{s,p,q,\nu} = \sum_{j=0}^{q-1} \exp\left(\frac{2\pi i p s j^2}{q} + \frac{2\nu m j}{q}\right)$$

where $s = a, b, c$

$$S_{s,p,q} = S_{s,p,q,0}$$

Lemma 1 $S = S_{s,p,q,\nu} = O(\sqrt{q})$

Proof

$$|S|^2 = \sum_{m=0}^{q-1} \sum_{t=0}^{q-1} \exp\left(\frac{2\pi i p s (m^2 - t^2)}{q} + 2\nu m (m - t)\right)$$

Put $m = t + r$, where r runs over q incongruent values (mod q)

$$|S|^2 = \sum_{t=0}^{q-1} \sum_r \exp\left(\frac{2\pi i p s (2rt + r^2)}{q} + 2\nu m r\right) \\ = \sum_r \exp\left(\frac{2\pi i p s r^2}{q} + \frac{2\nu m r}{q}\right) \sum_t \exp\left(\frac{4\pi i p t r s}{q}\right)$$

Now
$$\sum_t \exp\left(\frac{4\pi i p t r s}{q}\right) = 0 \quad \text{if } 2prs \not\equiv 0 \pmod{q} \\ = q \quad \text{if } 2prs \equiv 0 \pmod{q}$$

Hence since $2prs \equiv 0 \pmod{q}$ at most $2s$ times ($0 \leq r \leq q-1$) it is clear that

$$|S|^2 = O(q)$$

Lemma 2. On $\xi_{p,q}$ we have (for $s = a, b, c$)

$$g(w^s) = A_s + B_s$$

where $A_s = \sqrt{\frac{\pi}{s}} \frac{S_{s,p,q}}{q} \left(\frac{1}{n} - i\theta\right)^{-\frac{1}{2}}$

$$B_s = \frac{2}{q} \sqrt{\frac{\pi}{s}} \left(\frac{1}{n} - i\theta\right)^{-\frac{1}{2}} \sum_{\nu=1}^{\infty} S_{s,p,q,\nu} \exp\left(\frac{-\pi^2 \nu^2}{Sq^2 \left(\frac{1}{n} - i\theta\right)}\right)$$

and $g(w) = 1 + 2w + 2w^4 + 2w^9 + \dots$ more ($|w| < 1$)

Proof See Kloosterman "On the representation of numbers in the form $ax^2 + by^2 + cz^2 + dt^2$ " in *Acta Mathematica*, Vol 49, lemma 7, p 437

Lemma 3 $\sum_{m=1}^n r^2(m) = O(n^2)$

Proof Now,

$$\frac{1}{2\pi} \int_0^{2\pi} |f(\rho e^{i\theta})|^2 d\theta = \sum_{m=0}^{\infty} r^2(m) \rho^{2m}$$

Take $\rho = e^{-\frac{1}{n}}$. Then

$$\text{r.h.s.} \geq r^2(1) e^{-\frac{2}{n}} + r^2(2) e^{-\frac{4}{n}} + \dots + r^2(n) e^{-2} \geq e^{-2} \sum_{1 \leq m \leq n} r^2(m)$$

and hence the lemma is proved if

$$\int_0^{2\pi} |f(\rho e^{i\theta})|^2 d\theta = O(n^2)$$

On $\xi_{\rho, q}$

$$|A_s| = O\left[\frac{\sqrt{q}}{q} \left(\frac{1}{n^2} + \theta^2\right)^{-\frac{1}{2}}\right]$$

By lemma 1

$$|B_s| = O\left[\left(\frac{1}{n^2} + \theta^2\right)^{-\frac{1}{2}} \frac{1}{\sqrt{q}} \sum_{v=1}^{\infty} \left| \exp\left(\frac{-\pi^2 v^2}{sq^2 \left(\frac{1}{n} - i\theta\right)}\right) \right| \right]$$

Now,

$$\begin{aligned} \left| \frac{-\pi^2 v^2}{sq^2 \left(\frac{1}{n} - i\theta\right)} \right| &= e^{-R\left(\frac{\pi^2 v^2}{sq^2 \left(\frac{1}{n} - i\theta\right)}\right)} \\ &= e^{-R\left\{\frac{\pi^2 v^2 \left(\frac{1}{n} + i\theta\right)}{sq^2 \left(\frac{1}{n^2} + \theta^2\right)}\right\}} = e^{\frac{-\pi^2 v^2}{nsq^2 \left(\frac{1}{n^2} + \theta^2\right)}} \end{aligned}$$

Since $\frac{-2\pi}{q(q+q')} < \theta < \frac{2\pi}{q(q+q')}$ and $q+q' \geq \sqrt{n}$, $q+q'' \geq \sqrt{n}$ and

therefore $\theta^2 \leq \frac{4\pi^2}{q^2 n}$ it follows that

$$\frac{1}{nq^2 \left(\frac{1}{n^2} + \theta^2\right)} > \frac{1}{nq^2 \left(\frac{1}{n^2} + \frac{4\pi^2}{q^2 n}\right)} > \text{Min}\left(\frac{n}{2q^2}, \frac{1}{8\pi^2}\right) > \text{Min}\left(\frac{1}{2}, \frac{1}{8\pi^2}\right)$$

(Using $\frac{1}{a+b} > \text{Min}\left(\frac{1}{2a}, \frac{1}{2b}\right)$ provided $a, b > 0$) and $q < \sqrt{n}$.

Hence

$$\left| \frac{-\pi^2 \nu^2}{e^{sq^2 \left(\frac{1}{n} - i\theta\right)}} \right| \leq e^{\frac{-\pi^2 \nu^2}{8sq^2}} = e^{\frac{-\nu^2}{8s}}$$

Hence

$$\sum_{\nu=1}^{\infty} \left| \frac{-\pi^2 \nu^2}{e^{sq^2 \left(\frac{1}{n} - i\theta\right)}} \right| = 0 \quad (1)$$

and therefore

$$|B_s| = 0 \left(\frac{1}{\left(\frac{1}{n^2} + \theta^2\right)^{\frac{1}{2}}} \frac{1}{\sqrt{q}} \right)$$

From lemma 2 it follows that on $\xi_{p,q}$

$$g(w^s) = 0 \left(\frac{1}{\sqrt{q}} \frac{1}{\left(\frac{1}{n^2} + \theta^2\right)^{\frac{1}{2}}} \right).$$

But taking $\rho = e^{-\frac{1}{n}}$, $\lambda = \theta + \frac{2\pi p}{q}$

$$\begin{aligned} \int_0^{2\pi} |f(\rho e^{i\lambda})|^2 d\lambda &= \sum_{\xi_{p,q}} \int_{\xi_{p,q}} |f(w)|^2 d\theta \\ &= 0 \left(\sum_{\xi_{p,q}} \frac{1}{q^2} \int_{\xi_{p,q}} \frac{d\theta}{\left(\frac{1}{n^2} + \theta^2\right)^{\frac{3}{2}}} \right) \\ &= 0 \left(\sum_{\substack{(\rho,q)=1 \\ \rho \leq q \\ q \leq \sqrt{n}}} \frac{1}{q^2} \int_{-\infty}^{\infty} \frac{d\theta}{\left(\frac{1}{n^2} + \theta^2\right)^{\frac{3}{2}}} \right) \\ &= 0 \left(\sum_{\substack{(\rho,q)=1 \\ \rho \leq q \\ q \leq \sqrt{n}}} \frac{1}{q^2} \int_{-\infty}^{\infty} \frac{n^2 d\phi}{n(1+\phi^2)^{\frac{3}{2}}} \right) = 0(n^2) \end{aligned}$$

Hence the lemma

Concluding Argument.

Let $M(x)$ denote the number of $y \leq x$ for which

$$y = a\xi_u^2 + b\xi_v^2 + c\xi_w^2$$

where the ξ 's form a set of increasing positive integers having positive density.

It will be shown that for $x > x_0$, $M(x) > c_2 x$ where c_2 is an absolute positive constant

Let $f(y)$ denote the number of ways in which $y = a\xi_u^2 + b\xi_v^2 + c\xi_w^2$. Then evidently,

$$\begin{aligned} f(y) &\leq r(y) \\ \sum_{y \leq x} f(y) &= \sum_{a\xi_u^2 + b\xi_v^2 + c\xi_w^2 \leq x} 1 \\ &< \sum_{a\xi_u^2 \leq \frac{x}{3}} 1 \sim \theta\left(\sqrt{\frac{x}{3a}}\right) \theta\left(\sqrt{\frac{x}{3b}}\right) \theta\left(\sqrt{\frac{x}{3c}}\right) \\ a\xi_u^2 &\leq \frac{x}{3} \\ b\xi_v^2 &\leq \frac{x}{3} \\ c\xi_w^2 &\leq \frac{x}{3} \end{aligned}$$

where $\theta(x)$ denotes the number of ξ 's which are less than and equal to x . By hypothesis,

$$\theta(x) > c_1 x \quad (x > x_0)$$

where c_1 is an absolute positive constant. So we have

$$\sum_{y \leq x} f(y) > c_2 x^{\frac{3}{2}}$$

where c_2 is an absolute positive constant.

Using Schwarz's inequality that if

$$\left. \begin{matrix} a_1, \dots, a_x \\ b_1, \dots, b_x \end{matrix} \right\} > 0$$

then

$$\sum_{y=1}^x a_y b_y \leq \sqrt{\sum_{y=1}^x a_y^2 \sum_{y=1}^x b_y^2}$$

and putting $a_y = f(y)$, $b_y = 1$ if $f(y) > 0$ otherwise $b_y = 0$ it is seen that

$$\sum_{y=1}^x a_y^2 = \sum_{y=1}^x f^2(y), \quad \sum_{y=1}^x b_y^2 = M(x).$$

Hence

$$c_2 x^{\frac{3}{2}} < \sum_{y \leq x} f(y) \cdot 1 \leq \sqrt{M(x) \sum_{y \leq x} f^2(y)}$$

$$\text{i.e., } c_2^2 x^3 < M(x) \sum_{y \leq x} f^2(y) < M(x) \sum_{y \leq x} r^2(y) < M(x) O(r^3)$$

$$\text{i.e., } M(x) > c_2 x$$

where c_2 is an absolute positive constant. Hence our theorem.

QUASI-BOOLEAN ALGEBRAS AND MANY-VALUED LOGICS.

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I THE classical calculus of propositions, found for instance in the *Principia Mathematica*, can be interpreted, as is well-known, as a *truth-value system*. This is done by attributing to each proposition p a truth-value $t(p)$ which is zero or unity according as p is false or true. If now $f(p, q, r, \dots)$ be any proposition which is formed from the propositions p, q, r, \dots by the operations of the calculus (that is, $\sim, +, \cdot$, and $>$), it is a condition to be satisfied by any truth-value system that f should be *categorical*, that is, that the truth-value $t(f)$ of f should *not* depend on the actual propositional arguments p, q, r, \dots but only on their truth-values, $t(p), t(q), t(r), \dots$. This is easily verified by inspection for the propositional calculus, for

$$t(p + q) = \text{Max} [t(p), t(q)]$$

$$t(p \cdot q) = \text{Min.} [t(p), t(q)]$$

$$t(\sim p) = 1 - t(p)$$

$$t(p > q) = \text{Max} [1 - t(p), t(q)]$$

The laws of the propositional calculus are those propositions $f(p, q, r, \dots)$, which are true whatever be the truth or falsity of p, q, r, \dots .

This idea has been generalised by Lukasiewicz and Tarski who have constructed a logic of propositions with $n + 1$ truth-values denoted for convenience by $0, \frac{1}{n}, \frac{2}{n}, \dots, \frac{n-1}{n}, 1$. The implication-relation C of the calculus is *defined* by.

$$\begin{aligned} t(p C q) &= 1 \text{ if } t(p) \leq t(q) \\ &= 1 - t(p) + t(q), \text{ if } t(p) > t(q). \end{aligned}$$

Two propositions p, q are logically equivalent when each implies the other; from the truth-value $t(p C q)$, this can happen only when p and q have the same truth-value, since

$$[t(p) \leq t(q)] [t(q) \leq t(p)] \supset t(p) = t(q)$$

Further, *negation* is defined by:

$$t(\sim p) = 1 - t(p)$$

Logical addition (\vee) and multiplication (\wedge) of propositions are now defined by .

$$p \vee q = p \text{ C } q \text{ C } q \text{ Df}$$

$$p \wedge q = \sim (\sim p \vee \sim q) \text{ Df}$$

The *meaning* of the operations C, \sim , \vee , \wedge thus defined should not be identified with the broad meaning given to these same operations in the two-valued calculus. As a matter of fact, \vee , \wedge , \sim can not have the ordinary meanings, *or*, *and*, and *not*, since the law of excluded middle and the law of contradiction do not hold, for

$$t(p \vee q) = t(p \text{ C } q \text{ C } q) \text{ by definition}$$

If $t(p) \leq t(q)$, $t(p \text{ C } q) = 1$, and therefore $t(p \text{ C } q \text{ C } q) = t(q)$

If $t(p) > t(q)$, $t(p \text{ C } q) = 1 - t(p) + t(q)$ and

$$t(p \text{ C } q \text{ C } q) = 1 - [1 - t(p) + t(q)] + t(q) = t(p)$$

Thus $t(p \vee q) = \text{Max } [t(p), t(q)]$ Similarly

$$\begin{aligned} t(p \wedge q) &= 1 - t(\sim p \vee \sim q) = 1 - \text{Max } [1 - t(p), 1 - t(q)] \\ &= \text{Min } [t(p), t(q)] \end{aligned}$$

In particular

$$t(p \vee \sim p) = \text{Max } [t(p), 1 - t(p)] \neq 1$$

$$t(p \wedge \sim p) = \text{Min } [t(p), 1 - t(p)] \neq 0$$

Thus the laws of excluded middle and contradiction both fail. The actual meaning to be attached to the operations of the many-valued calculus must be discovered from considerations of probability*. For, the limiting form when n becomes infinite, of the Łukasiewicz-Tarski logic is the logic of probability.

II. The purpose of this paper is not the investigation of the meaning of the operations of the many-valued calculus. It is on the other hand to arrive at a view of many-valued logics which is somewhat more general than that of Łukasiewicz and Tarski, and includes their extension as a special case. The view which I wish to advance is *the truth-values attributed to propositions in any propositional calculus must be elements of, what I shall call, a quasi-boolean algebra*. By a *boolean algebra* is meant an algebra which is constructed on the model of the algebra of all subclasses of a given class. By a *quasi-boolean algebra*, I shall mean an algebra which is constructed on the model of the algebra of all subclasses of a given class *containing groups of like elements*. This requires further explanation, as it is not evident as to what is meant by the algebra of all subclasses of a given class, when the class contains like elements. The explanation is supplied in what follows.

* For these meanings see Lewis I and II.

III The Simple Quasi-boolean Algebra

The *simple quasi-boolean algebra* may be defined to be an algebra constructed on the model of the algebra of all subclasses of a class, *all* of whose elements are alike. To study this algebra, consider a class C_n composed of n like elements. Since the elements of C_n are indistinguishable, two subclasses of C_n containing the same number r of elements are indistinguishable from one another. Hence C_n has precisely $n + 1$ subclasses, containing respectively 0, 1, 2, ..., n elements. Thus the subclasses are in (1, 1) correspondence with the integers $\leq n$, and are in linear order.

The *sum* and *product* of two subclasses c, c' are defined generally as the classes containing the elements of c, c' , and the elements common to c, c' , respectively. These definitions would however be ambiguous if applied to two subclasses c_r, c_s containing respectively r, s elements of C_n . To remove the ambiguity we consider the extreme cases of indetermination. We shall say that c_r, c_s are in the position of *maximum incidence*, when they have as many common elements as possible, and in the position of *minimum incidence*, when they have as few common elements as possible. The sum and product of c_r, c_s in the position of maximum incidence are defined to be their quasi-boolean *sum* and *product*. It follows from this definition, that if $r \leq s$,

$$c_r + c_s = c_r$$

$$c_r c_s = c_r$$

Hence also

$$c_0 + c_k = c_k, c_0 c_k = c_0$$

$$c_n + c_k = c_n, c_n c_k = c_k$$

The associative and commutative laws hold for these two quasi-boolean operations, as well as the existence of zero and the unit. Further, just as in boolean algebra, *each of these quasi-boolean operations distributes the other*.

For

$$c_r (c_s + c_t) = c_k, k = \text{Min} [r, \max (s, t)]$$

$$c_r c_s + c_r c_t = c_p, p = \text{Max} [\min (r, s), \min (r, t)]$$

We easily verify

$\text{Min} [r, \max (s, t)] = \text{Max} [\min (r, s), \min (r, t)]$, for any three integers r, s, t

Thus this distributive law and similarly the other distributive law are seen to hold.

The negative \bar{c}_r of the quasi-boolean element c_r is defined to be the subclass which remains when c_r is removed from C_n . It is clear that $\bar{c}_r = c_{n-r}$,

and $\bar{c}_r = c_r$ as in boolean algebra. Further with this definition of the negative, the principle of duality holds just as in boolean algebra For,

$$(\bar{c}_r + \bar{c}_s) = \bar{c}_k = c_{n-k}, \quad k = \max(r, s)$$

$$\bar{c}_r c_s = c_{n-r} \cdot c_{n-s} = c_{n-k}, \text{ since } n - k = \min(n - r, n - s).$$

Thus $(\bar{c}_r + c_s) = \bar{c}_r c_s$, similarly $(\bar{c}_r \bar{c}_s) = c_r + \bar{c}_s$

However, the two boolean laws $c_r + c_r = 1$, $c_r \cdot \bar{c}_r = 0$ no longer hold. We have in fact,

$$c_r + c_r = c_r + c_{n-r} = c_k, \quad k = \max(r, n - r)$$

$$c_r c_r = c_r c_{n-r} = c_l, \quad l = \min(r, n - r)$$

Further, in the simple quasi-boolean algebra we can define the relation 'contained in', ($<$) as follows

$$c_r < c_s \text{ means } c_r + c_s = c_s$$

Then, just as in boolean algebra, we can define the two quasi-boolean operations $+$ and \times in terms of the relation $<$ and its converse $>$, namely, $c_r + c_s$ is the element which contains c_r and c_s and which is contained in every element containing c_r and c_s , with a similar definition for $c_r \cdot c_s$. By means of the relation $<$, the simple quasi-boolean algebra is linearly ordered

IV The Group-operation of the Simple Quasi-boolean Algebra

We shall now shew that if we take the subclasses c_r, c_s in their position of minimum incidence, then the formation of their sum and product can be effectively combined into a single operation, which is a group-operation of the simple quasi-boolean algebra, and exhibits it as a cyclic group of order $n + 1$

For, if $r + s \leq n$, the classes, c_r, c_s have no common element in their position of minimum incidence, hence $c_r + c_s = c_{r+s}$, $c_r \cdot c_s = c_0$, while if $r + s > n$, the classes will have $r + s - n$ common elements in minimum incidence, so that $c_r + c_s = c_n$, $c_r \cdot c_s = c_{r+s-n}$. Discarding the trivial results c_0 and c_n , we see that sum and product in the position of minimum incidence can be combined into a single operation R such that.

$$c_r R c_s = c_k, \quad k = \text{least positive residue of } r + s \text{ mod } (n + 1)$$

Thus $c_r R c_s$ is the sum of c_r, c_s in the position of minimum incidence if $r + s < n + 1$, and is otherwise the largest proper subclass of the product of c_r, c_s (in minimum incidence). It is clear that R is a group-operation of period $n + 1$, and that the simple quasi-boolean is a cyclic group with respect to R. Contrary to what happens in boolean algebra, R cannot be expressed in terms of the quasi-boolean operations.

The definition of R is slightly more simple when n is infinite, namely $c_r R c_s = c_r + c_s$ or $c_r \cup c_s$ in the position of minimum incidence, according as Measure $(c_r) + \text{Measure}(c_s) < \text{or} \nless \text{Measure}(c_n)$

V The General Quasi-boolean Algebra

The general quasi-boolean algebra may be defined as the vector compound of any number of simple quasi-boolean algebras, S_1, S_2, \dots . If s_i is an element of S_i , the quasi-boolean operations for the vectors

$$\sigma = (s_1, s_2, \dots), \sigma' = (s_1', s_2', \dots)$$

are defined by

$$\begin{aligned} \sigma &= (\bar{s}_1, \bar{s}_2, \dots), \sigma + \sigma' = (s_1 + s_1', s_2 + s_2', \dots) \\ \sigma\sigma' &= (s_1 s_1', s_2 s_2', \dots) \end{aligned}$$

It is clear that $\sigma > \sigma'$ only if each $s_i > s_i'$

A simple example of the finite quasi-boolean algebra is the algebra (which has been known for a long time) of divisors of a number $N = p_1^{n_1} p_2^{n_2} \dots p_r^{n_r}$, where the p 's are distinct primes. The quasi-boolean sum and product of two divisors d_1, d_2 of N , are respectively their greatest common divisor and their least common multiple. The quasi-boolean negative of any divisor d is the conjugate divisor $\frac{N}{d}$. The divisors of N represent in fact subclasses of a class with n_1 like elements p_1 , n_2 like elements p_2, \dots, n_r like elements p_r . It may be shewn that the number of elements in the general finite quasi-boolean algebra must be of the form $d(N)$ (= number of divisors of N) and that the algebra is identical with the algebra of divisors of N .

More generally, it may be shewn that a set of elements with a reflexive transitive relation $<$, and a negation operation (\bar{a}), is a quasi-boolean algebra, if the following postulates hold.

- (1) $a < b \rightarrow b < a \rightarrow a = b$
- (2) $a < b \rightarrow b < \bar{a}$
- (3) $\bar{\bar{a}} = a$
- (4) For any two elements a, b there exists a unique element x , such that $a < x, b < x, a < c \cdot b < c \rightarrow x < c$

We write $x = a + b$

- (5) There exists two distinct elements 0, 1, such that

$$0 < x < 1 \text{ for every element } x$$

- (6) $a(b + c) = ab + ac$, where the product is defined by $xy = \overline{(x + y)}$.

(7) A postulate for ensuring that the elements of a simple quasi-boolean algebra are in linear order.

The quasi-boolean algebra may be split up into its simple quasi-boolean components, by a theory of minimal elements as in the case of the boolean algebra

VI The Truth-value System

Consider a logic of propositions with an implication-operation \mathbf{C} . Whatever be the *meaning* of implication, the relation of implication must be reflexive and transitive, and must be related to *dema*l in such a way that $p \mathbf{C} q$ is logically equivalent to $\sim q \mathbf{C} \sim p$. Assume further two logical operations \vee and \wedge (corresponding to *or*, and *and*), with the properties

$$p \mathbf{C} p \vee q, q \mathbf{C} p \vee q,$$

$$p \mathbf{C} r, q \mathbf{C} r \mathbf{C} p \vee q \mathbf{C} r,$$

(with similar properties of \wedge). In the Łukasiewicz-Tarski logics $p \vee q$ is defined in terms of \mathbf{C} as $p \mathbf{C} q \mathbf{C} q$

If we attribute to the propositions p of the calculus, a system of truth-values $[t(p)]$, we have to require that the logical relations and operations should be exactly imaged in corresponding relations and operations in the system $[t(p)]$ of truth-values. Hence the system $[t(p)]$ admits a reflexive transitive relation $<$ corresponding to \mathbf{C} , a unary operation of negation, corresponding to *dema*l, and standing in such relation to $<$ that $t_1 < t_2$ is equivalent to $t_2 < t_1$, and further two operations $+$ and \times , which can be defined in terms of $<$, by means of

$$p < p + q, q < p + q,$$

$$\text{If } p < r \text{ and } q < r, \text{ then } p + q < r,$$

with similar definitions for $p \times q$

These facts shew that the general features of the structure of the system of truth-values, are such as to render the system a quasi-boolean algebra

When the quasi-boolean algebra is a *simple* one, we have the truth-value system of Łukasiewicz and Tarski

When the quasi-boolean algebra reduces to a two-element boolean algebra (which is a particular case of the simple quasi-boolean algebra), we have the ordinary or classical two-valued logic

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COEFFICIENT OF VISCOSITY OF AIR.

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THE determination of the coefficient of viscosity of air has become of special interest within the last few years since the suggestion of Shiba¹ (1932) that an error in the adopted value of this quantity was responsible for the discrepancy between the values of electronic charge determined by the oil-drop and X-ray methods. Since then, Kellstrom² (1937), Bond³ (1937), Houston⁴ (1937) and Rigden⁵ (1938) have determined the value of the coefficient of viscosity, either by the capillary tube method or by the rotating-cylinder method. Their results when substituted in Millikan's data for determining the electronic charge, gives a value for " e " which is in fair agreement with the value of the same constant as determined by X-ray method. In 1923, Wagstaff⁶ suggested a method of measuring this coefficient and in these investigations, his apparatus and method have been improved. The results of the preliminary experiments made with the improved apparatus were published⁷ in 1936, but the apparatus was further improved, and the results obtained are given in this paper.

I Experimental Arrangement and General Method of Work

The apparatus used in these experiments for measuring the viscosity coefficient of air does not differ in principle from the one used by Wagstaff, but devices to dehydrate the gas and to measure automatically the time during which the gas flows through a capillary tube have been added. An arrangement to keep the gas at constant (atmospheric) pressure has also been devised.

The apparatus may be said to consist of four parts, namely, (1) the exhaust chamber, (2) the reservoir of gas, (3) the dehydrating system for gases, and (4) the automatic device for measuring time intervals.

The general lay-out of the apparatus is shown in the figure and the inset shows details of the holder for the microscope cover-slip.

(1) *The Exhaust Chamber*—Wolfe's bottles A and B form the exhaust chamber and their total volume is about 5,000 c.c. In the mouth of the bottle A is placed the holder for clamping the microscope cover-slip. It is a tightly fitting brass tube which is threaded at its upper end on its outer

surface On top of this tube is placed a thick copper-plate with an aperture of radius 0.79 cm Due care was taken that the centre of the plate was on the axis of the tube Over this plate a microscope cover-slip of thickness 0.0225 cm was placed, and the latter was tightly clamped by screwing a brass-cap over the tube This brass cap had an aperture of radius 0.79 cm, which coincided with the aperture of the plate Thus an area of 0.79 cm diameter was acted on by the difference of pressures of the atmosphere and that within the exhaust chamber

An optically plane circular plate of the same diameter as the exposed part of the cover-slip was placed in the cap over the cover-slip Newton's rings formed according to ordinary arrangements were observed by a microscope Any change of pressure within the exhaust chamber changed the sag of the cover-slip and the number of Newton's rings that converged towards the centre were counted from which the change of pressure was calculated according to Wagstaff's formula

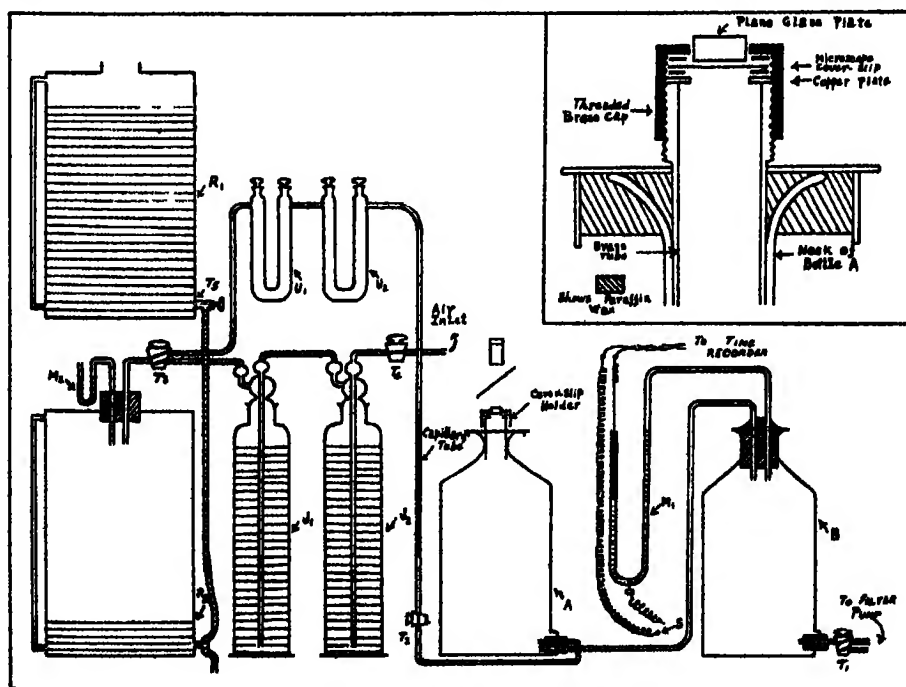
(2) *The Reservoir of Gas*— R_1 and R_2 , the reservoirs of liquid paraffin oil and gas respectively, are cylindrical copper vessels of about 6 litres capacity and tinned inside As the gas in R_2 is at atmospheric pressure and that in the exhaust chamber is below that pressure, gas flows out from R_2 through U_1 and U_2 and the capillary tube, to the exhaust chamber Thus, the pressure within R_2 should in the ordinary course decrease, but in this arrangement, paraffin oil flows from R_1 to R_2 and the gas remaining in the latter reservoir is compressed, and the flow of paraffin is so adjusted (by means of the tap T_2) that the pressure remains nearly constant (atmospheric) The manometer M_2 , which contains liquid paraffin oil, shows the change in pressure, if any, in R_2 The use of liquid paraffin is preferable on account of its low coefficient of viscosity and also because its vapour pressure is negligible compared with other equally viscous liquids It is interesting to find that Bond³ has also used paraffin oil for the same reasons, although it may be pointed out that this liquid was used even in the initial experiments the results of which were published in September 1936

(3) *The Dehydrating System for Gases*—Air is led to the apparatus through sulphuric acid in jars J_1 and J_2 and is stored in the vessel R_1 Air is then led to the exhaust chamber through the CaCl_2 tubes U_1 and U_2 and the capillary tube Thus air passing through the capillary tube is dehydrated as far as is possible

(4) *Automatic Device for measuring Time Intervals*—The manometer M_1 serves a double purpose—firstly, it shows the initial pressure to which the cover-slip is subjected and secondly, it serves to complete the electrical circuit which operates the time recorder A platinum electrode is fused in

the bend of the U-tube of the manometer, and a thick copper wire capable of sliding in one arm of the tube forms the other electrode. These electrodes, together with an accumulator, a pair of magnet-coils and a switch are all connected in series. The magnet-coils are from an electric bell, from which the make-and-break contacts are removed and the armature carries a sharp lead pencil which can press against a drum which rotates at a very steady rate by means of a clockwork. The pencil point draws a line on the paper wrapped around the drum, only when mercury in the manometer M_1 completes the electrical circuit. The magnet-coils are mounted on a carriage which can move horizontally on guide-rails. By means of a mechanical arrangement, the carriage moves horizontally simultaneously as the chronometer drum revolves. Thus, the pencil point actually draws a spiral on the paper, and by previous calibration the length of the line gives the time interval during which the current was allowed to pass through the magnet-coils.

On an inspection of the general lay-out of the apparatus, it will be noticed that even if the switch S is closed, current will not be fed to the time



General lay-out of the apparatus. Inset shows details of cover-slip holder.

A, B —Wolfe's bottles; J_1, J_2 — H_2SO_4 dehydrating jars, M_1, M_2 —Manometers; R_1 —Reservoir of Paraffin Oil; R_2 —Reservoir of air; S —Switch, T_1, T_2, T_3, T_4 —Glass taps; T_5 —Water tap; U_1, U_2 — $CaCl_2$ tubes.

recorder if mercury does not complete the electrical circuit between the platinum electrode and the thick copper electrode placed in the open limb of the manometer M_1 . Thus the current is fed to the time recorder as soon as mercury rises to a predetermined height in the open limb of the manometer, which can be adjusted by moving the thick wire up or down, as required. Again, as soon as the coils are energised by the flow of current through them, a light tick is heard as the pencil point is pressed against the chronometer drum, which gives the signal to the observer to begin counting the rings which converge towards the centre, as seen through the microscope. Thus this arrangement is automatic because the time recorder is put into action as soon as a predetermined pressure is reached in the exhaust chamber and the observer has only to open the switch to break the electrical circuit, after a given number of Newton's rings have converged to the centre, the time interval being marked on the paper.

After the apparatus had been set up, a special experiment was performed to determine Young's Modulus for glass of cover-slip, using Wagstaff's formula, which is,

$$E = \frac{15 R^4 p'}{128 t^3 N \lambda}$$

where "E" denotes Young's Modulus, "t" the thickness of the cover-slip, "R" the radius of the surface of the cover-slip subjected to pressure, "p'" being the change in pressure when "N" Newton's rings of wave-length " λ " converge towards the centre. The value of "E" for glass of the cover-slip used in these experiments was 5.8×10^{11} dynes per sq cm, and incidentally this experiment also gave the value of the ratio p'/N as being 0.2136 cm of mercury per Newton's ring, that is, that if a Newton's ring converged towards the centre, the pressure changed by 0.2136 cm of mercury.

When an observation was to be taken, the reservoir R_2 was first completely filled with paraffin oil and the reservoir R_1 , which was empty, was placed at a lower level than the former. Paraffin oil is then made to flow from one of the tubes attached to the Y-shaped tube of the reservoir R_2 to the reservoir R_1 . The glass tap T_4 is then opened to the atmosphere and as paraffin oil flowed out from the reservoir R_2 , its place was taken by air. Thus when the cylinder contained no paraffin, it was full of dehydrated air.

The pressure in the exhaust chamber was then reduced by means of the filter pump and the relative heights of the mercury columns in the two limbs of the manometer M_1 were measured by means of a carefully adjusted cathetometer. The thick wire in the open limb of the manometer was then so adjusted that its point just touched the surface of the mercury column

in that limb. With the adjustment of the initial pressure, the barometer was also read, as well as the thermometer.

The flow of paraffin oil was so adjusted that the mean pressure during the experiment (in the reservoir R_2) remained at nearly the atmospheric pressure and also that the difference from this pressure was as small as possible. The tap T_3 was left untouched and a pinch-cock stopped the flow of paraffin.

The pressure within the exhaust chamber was then reduced to a value slightly less than the predetermined initial pressure to accustom the eye of the observer to the passage of Newton's rings and also to be ready to begin the count as soon as the initial pressure was reached.

The tap T_2 near the capillary tube was then opened (the pinch-cock on the rubber tube connecting the two reservoirs having already been removed), gas flowed from R_2 to the exhaust chamber and the pressure within the latter increased, and Newton's rings were seen to converge towards the centre. As soon as the predetermined initial pressure was reached in the exhaust chamber, the time recorder came automatically into action.

After the required number of rings had converged towards the centre, the tap near the capillary tube was closed and the pinch-cock again applied to the rubber tube to stop the flow of paraffin oil. Of course, the electrical circuit had already been broken by means of the switch S , when the last ring disappeared.

II The Formula Used in Calculations

The formula used in the determination of the coefficient of viscosity is the same as that given by Wagstaff, namely,

$$\eta = \frac{\pi a^4 T}{8lS} \cdot \frac{p_2}{\log_e \left\{ \frac{p_2 + p_1 + p'}{p_2 - p_1 - p'} \cdot \frac{p_2 - p_1}{p_2 + p_1} \right\}},$$

where the gas of viscosity " η " flows through a capillary tube of length " l " and of radius " a ", the total volume of the apparatus being " S ", the pressure difference at the two ends of the capillary tube is " $p_2 - p_1$ " initially, " p_2 " being the atmospheric pressure, the gas having flowed for a time " T " during which the initial pressure has changed by an amount " p' ", the latter being given by the formula on page 174.

The total volume of the apparatus, " S ", was determined by filling the whole exhaust chamber from the tap T_1 to the tap T_2 with distilled water, and then measuring its volume.

The various constants for the apparatus used in these experiments were as follows .—

Thickness of cover-slip $\approx t = 0.0225$ cm

Radius of aperture in cap of the cover-slip holder $\approx R = 0.79$ cm

Young's Modulus for glass of cover-slip (determined from experiment)

$$\approx E = 5.8 \times 10^{11} \text{ dynes per sq cm}$$

Total volume of the apparatus $\approx S = 5,045$ cc

Capillary tubes of different lengths and bores were used (four different tubes).

III Results

In these experiments, the mean of three readings of the time interval for a given number of rings at a fixed initial pressure was used for calculations, and the value of the viscosity coefficient of air was determined from each separate reading, which corresponded to a particular temperature. The value so obtained was corrected for temperature by using the formula due to Millikan⁸ (1913), namely,

$$\eta_{23^\circ \text{C}} = \eta_{\theta^\circ \text{C}} + 0.000000493 (23 - \theta),$$

where $\eta_{23^\circ \text{C}}$ stands for the coefficient of viscosity of air at 23°C and $\eta_{\theta^\circ \text{C}}$ for the same coefficient at $\theta^\circ \text{C}$.

A typical set of readings (using capillary tube No 3, $l = 22.45$ cm, and $a = 0.02378$ cm) is given in Table I.

TABLE I *Temperature = 31.4°C*

$p_2 - p_1$ cm of Hg	p_2 cm of Hg	p_1 cm of Hg	N	T secs	$\eta \times 10^7$ c g s units
12.62	76.38	63.76	5	16.0	1878.57
			10	33.3	1871.78
			15	52.5	1876.04
			20	73.7	1874.28
			25	97.6	1872.66
			30	125.4	1876.12
			35	158.0	1876.07
			40	198.0	1876.76
			45	250.0	1878.46

Mean value of $\eta_{31.4^\circ \text{C}} = 1875.94 \times 10^{-7}$ c g s. units.

Calculated value of $\eta_{23^\circ \text{C}} = 1834.528 \times 10^{-7}$ c g s. units

In Table II is given the summary of results obtained in these experiments

TABLE II

Temperature $\theta^{\circ}\text{C.}$	$\eta_{\theta^{\circ}\text{C}} \times 10^7$ c g s units	$\eta_{20^{\circ}\text{C}} \times 10^7$ c g s units
28 8	1863 05	1834 456
28 6	1862 48	1834 842
28 6	1861 80	1834 292
29 2	1864 71	1834 144
29 6	1867 06	1834 522
31 4	1875 94	1834 528
28 2	1859 96	1834 324
29 4	1865 86	1834 134
27 0	1853 91	1834 185
27 2	1855 35	1834 644
28 6	1862 02	1834 412
29 0	1863 81	1834 230

The mean value of the readings in the last column gives $\eta_{20^{\circ}\text{C}} = 1834.38 \times 10^{-7}$ c g s units with a variation of $\pm 0.35 \times 10^{-7}$ c g s units. Thus the mean of 94 independent readings gives the value, $\eta_{20^{\circ}\text{C}} = (1834.38 \pm 0.35) \times 10^{-7}$ c g s units

The value of η when substituted in Millikan's original data, in place of Harrington's value, gives the value of the electronic charge,

$$e = \frac{(18344)^{\frac{1}{2}}}{(18226)} \times 4.77 \times 10^{-10} \text{ e s. units}$$

$$= 4.816 = 10^{-10} \text{ e s. units}$$

Thus, it has been possible to show that the use of this apparatus in the determination of the coefficient of viscosity of air can lead to accurate value of this constant, which in turn gives a very good value of the electronic charge which agrees quite closely with the value found by other methods.

The authors have to express their sincere thanks to Prof G R. Paranjpe, Head of the Department of Physics, Royal Institute of Science, Bombay, for the valuable suggestions given by him during the course of the experiments and also for the keen interest shown by him in the work

Thanks are also due to Dr T S Wheeler, Principal, Royal Institute of Science, Bombay, for giving us all facilities to carry out this work

Summary

Using a modified form of Wagstaff's apparatus for measuring the coefficient of viscosity of air by the method of interference fringes and using capillary tubes, the value of $\eta_{21^{\circ}\text{C}}$ has been found to be $(1834.38 \pm 0.35) \times 10^{-7}$ c.g.s. units. The value of the electronic charge, e , calculated with this value of η is 4.816×10^{-10} e.s. units. Both these values are in close agreement with those obtained recently by other workers using different methods.

Addendum

There is a note by Bannerjea and Pattanaik in *Nature* (4th June 1938, 141, 1016) on "Viscosity of Air and Electronic Charge". A similar note was published by the authors in *Current Science* (Majumdar and Vajifdar, *Current Science*, 1936, 5, 133)

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STUDIES IN TURBINE GEOMETRY—II. ON THE SUB-GEOMETRIES OF LIE WHICH BELONG TO THE MOBIUS-LAGUERRE PENCIL.

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Received September 5, 1938

1 WE have seen in the first paper of this series¹ that the totality of turbines in a metrical S_n may be represented by the points of a projective S_{n+1} , the oriented spheres (which are particular turbines whose Mobius- and Laguerre-spheres coincide) corresponding to points on the Lie quadric

$$\Omega(X, X) = -x_0^2 + x_1^2 + \dots + x_{n+1}^2 - x_{n+2}^2 = 0 \quad (1.1)$$

The Projective Group in S_{n+1} which keeps Ω invariant (the Lie Group) is associated in the sense of Klein's Erlanger programme with Lie Geometry which is the invariant theory of transformations which carry turbines into turbines and oriented spheres into oriented spheres and conserve proper contact. Among the sub-geometries of Lie's geometry only two have received detailed attention, namely, those associated with the sub-groups of the Lie Group which have the prime $x_0 + x_1 = 0$ corresponding to spheres of infinite radius, and the prime $x_{n+1} = 0$ corresponding to spheres of zero radius as invariant primes. The former of these is Laguerre's geometry of oriented lines and spheres, and the latter is the one based on the inversion group and may be called Inversion Geometry or Mobius Geometry.

In this paper it is proposed to discuss the main features of the sub-geometries of Lie obtained by taking any one of the pencil of primes $k(x_0 + x_1) + x_{n+1} = 0$ as an invariant variety, and to obtain a principle of transference by which any result of Mobius Geometry may be associated with a corresponding result in any other Geometry of the Mobius-Laguerre pencil. While the existence of these geometries is hinted² in Prof. Blaschke's monumental work *Vorlesungen über Differentialgeometrie* of which the third volume is devoted to circle and sphere geometries, the introduction of the turbine concept is a powerful help in giving concreteness and reality to these geometries.

¹ "The concepts of Turbine Geometry," *Journal of the Indian Mathematical Society*, 1938, Vol. III, No. 3. This paper will be referred to as T.G.I. The reference here is to T.G.I., para 4.

² Blaschke, *Differentialgeometrie*, III, 1929, p. 208.

Invariant Concepts of G_k .

2 We define the geometry G_k as the invariant theory of the $(n+1)(n+2)/2$ parameter group of projective transformations which carry Ω into itself and have the prime

$$\pi_k \equiv \Omega(X, K) \equiv k(x_0 + x_1) - x_{n+1} = 0 \quad (2.1)$$

as an invariant prime and hence also its pole $K \equiv (-k, k, 0, 0, \dots, 0, 1)$ as an invariant point. The geometries G_0 and G_∞ corresponding to $k=0$ and $k \rightarrow \infty$ are the geometries of Möbius and Laguerre respectively.

On the algebraic side, the determination of a complete system of invariants of a system of n oriented spheres or turbines is equivalent to the determination of the invariants of one quadratic form and a set of $n+1$ linear forms in cogredient variables, one associated with each turbine (by polarisation wrt Ω), and the invariant form (2.1).

In this geometry, oriented spheres of radius k play a peculiar rôle so that it is convenient to have a special name for them. We call them k -spheres. We shall also use a prefix k attached to any concept of Möbius or Laguerre geometry to denote the corresponding concept of G_k , e.g., k -inversion.

Corresponding to the angle and the tangential segment which are invariant respectively in G_0 and G_∞ , we have here a basic invariant which can be expressed either in terms of an angle or of a length which we proceed to define. Consider two surface elements of a k -sphere. These determine two points P, Q and also two oriented primes p, q , one through each point. The angle $\pm \theta$ between the oriented primes is determinate mod 2π and will be called the "angle between the two surface elements". The arc length $\pm s$ between the points P, Q measured along the great circle through PQ is also determinate mod $2\pi k$ and will be called "the arc segment" between the oriented surface elements. They are connected by the relation that the latter is k times the former.

3 Firstly we notice that $x_{n+1}/(x_0 + x_1) = r$ the oriented radius of the inner sphere of the turbine X . From (2.1) we see that

the transformations of G_k carry every turbine of inner radius k into another turbine of inner radius k . In particular they carry oriented spheres of radius k into oriented spheres of radius k (3.1)

We have seen that in Lie's geometry and hence also in its sub-geometries proper contact is conserved and hence that these are essentially geometries of surface elements. It is thus important to know how the surface elements of a k -sphere are carried over into the surface elements of the transformed k -sphere. Taking n neighbouring k -spheres, these are carried over into n

neighbouring k -spheres. In the limiting position n such spheres have in common a pair of diametrically opposite surface elements. Thus a pair of diametrically opposite elements of a k -sphere correspond to a pair of diametrically opposite surface elements of the transformed k -sphere. From this follows easily the following basic theorem of G_k geometry

The angle and the arc segment between two surface elements of a k -sphere are invariants in the geometry G_k (3.2)

If we take two oriented spheres we can in general find a k -sphere S having proper contact with both. The transformations of G_k carry the two spheres into two others which touch S' the k -sphere which is the transform of S . Applying (3.2) to the two contact surface elements and their transforms, we see that

the angle and the arc segment between the surface elements in which a k -sphere touches two oriented spheres are invariants in G_k (3.3)

In G_0 (Mobius Geometry) the arc segment is of zero length and the angle (angle of intersection) is the only invariant. On the other hand, in G_∞ (Laguerre Geometry) the angle is zero and the arc segment becomes the common tangential segment.

4. The Fundamental Involution I Associated Spheres and Turbines

The involution I (projective transformation of period two) which has K for a fixed point and its polar prime π_k for fixed prime carries Ω into itself and is called the fundamental involution I of G_k . It associates oriented spheres in pairs in such a manner that the tangent primes at the corresponding points on Ω meet on π_k . Interpreting this we have the result

Two "associated spheres" S, S' which correspond to points on Ω collinear with K have the property that each is the envelope of k -spheres touching the other. Hence the spheres S, S' are concentric and the sum of their radii is $2k$ (4.1)

In G_0 (Mobius Geometry) two associated spheres differ only in orientation, while in Laguerre Geometry the associate of every sphere is the point sphere l at infinity (vide TGI 4.5)

We have seen in TGI para 2, that a turbine may be defined by means of its inner sphere c and the tangential segment t or through its outer sphere C and the angle α , these two specifications using respectively the invariant concepts of G_0 and G_∞ respectively. Exactly in the same way, we may define a turbine in terms of the concepts of G_k as follows. All the k -spheres which touch a turbine have for envelope two "associated spheres" S, S' whose radii are $k + \rho$ and $k - \rho$ where

$$\rho^2 = \{t^2 + (r - k)^2\}. \quad (4.2)$$

To obtain the turbine (c, t) , we take every oriented surface element of S and slide it along the unique k -sphere through it in all directions so that it makes a constant angle β with its old position, in other words move it through a constant arc segment $k\beta$ —where

$$\tan \beta = t/(r - k) \quad (4.3)$$

The same turbine may also be obtained by treating the surface elements of S' in a similar manner the angle and the arc segment being, however, now $(\pi - \beta)$ and $k(\pi - \beta)$. If the angles (or the arc segments) to be taken with S and S' be interchanged, we shall get another turbine which is the transform of the original turbine in the involution I . Two such turbines correspond to points in S_{n+2} collinear with K and separated harmonically by K and π_k . When β is a right angle, the two turbines coincide and the point lies on π_k so that the inner radius of the turbine is k . From the equality of the arc segments $k(\pi - \beta)$ and $k\beta$ we deduce that

When a k -sphere touches a k -turbine (a turbine whose inner radius is k), its section with the outer sphere of the latter is a diametral section of the k -sphere (4.4)

In such a case we say that the k -sphere is bisected by the outer sphere of the turbine. In the correspondence which we shall be later setting up between G_0 and G_k , non-oriented spheres of radius k correspond to points and their bisection by other spheres to the incidence relation of points and spheres (*vide* para 7).

Since by (3.2) the angles β or $\pi - \beta$ either of which may be used to specify the turbine are invariants in G_k , it may be expected that $\tan^2 \beta$ will be an absolute invariant of the turbine under the transformations of G_k .

5. Invariants of a System of Turbines.

For real transformations of the Lie group a single turbine X has but one invariant—the sign of $\Omega(X, X)$. If this is positive $R^2 - r^2 = t^2$ is positive and t is real, if it is negative $R^2 < r^2$ and t is imaginary.

In G_k a turbine X has a single absolute invariant, namely

$$\Omega(K, X)^2 / \Omega(X, X) \cdot \Omega(K, K) = -(r - k)^2 / t^2 \quad (5.1)$$

which represents the square of the cosine of the non-Euclidian separation of the points K and X with Ω as the absolute quadric. Its value is $-\cot^2 \beta$ where β is the angle mentioned in the previous para. When the invariant (5.1) vanishes $\beta = \pi/2$ and the turbine has an inner radius k . When it becomes infinite $\beta = 0$ and the turbine is a sphere.

For two turbines $X_1 = (c_1, t_1)$ and $X_2 = (c_2, t_2)$ we have, besides their separate invariants $\cot^2 \beta_1$ and $\cot^2 \beta_2$ a joint invariant in Lie's Geometry

and hence also in its sub-geometries, namely

$$\Omega(X_1 X_2)^2 / \Omega(X_1 X_1) \Omega(X_2 X_2) = (t_{12}^2 - t_1^2 - t_2^2) / 4t_1^2 t_2^2, \quad (5.2)$$

where t_{12} is the length of the common tangential segment of c_1 and c_2 . If both the turbines are of inner radius k , we have a simple geometrical interpretation for the joint invariant (5.2). We take a k -sphere which has proper contact with both the k -turbines X_1, X_2 and which is therefore cut by their outer spheres in diametral prime sections which are respectively perpendicular to the lines joining its centre with those of the turbines. The triangle formed by the three centres has sides t_1, t_2 and t_{12} and hence the invariant (5.2) is the square of the cosine of the angle between the two diametral primes. Since the first member of (5.2) represents the square of the cosine of the non-Euclidean separation of X_1 and X_2 with respect to the absolute Ω , we see that

we may identify the non-Euclidean separation of the points representing two k -turbines with the angle between the two diametral prime sections of a k -sphere touching both the turbines, along which it is cut by the outer spheres of the two turbines (5.3)

If the given turbines have an inner radius other than k , we have under G_k an absolute invariant

$$\begin{aligned} \Omega(X_1 X_2) \Omega(K K) - \Omega(X_1 K) \Omega(X_2 K) \\ &= (t_{12}^2 - t_1^2 - t_2^2) - (k - r_1)(k - r_2) \\ &= (d^2 - r_1^2 - r_2^2 + 2r_1 r_2 - t_1^2 - t_2^2) - (k - r_1)(k - r_2) \\ &= 2 + [d^2 - (r_1 - k)^2 - (r_2 - k)^2 - t_1^2 - t_2^2] - (r_1 - k)(r_2 - k) \end{aligned} \quad (5.4)$$

where d is the distance between the centres of X_1 and X_2

When the two turbines are spheres, t_1 and t_2 vanish and $r_1 - k, r_2 - k, d$ are the sides of a triangle formed by the centres of the spheres and of a k -sphere which has proper contact with both of them. Hence the invariant (5.4) is $4 \sin^2 \lambda / 2$ where λ is the angle subtended at the centre of the k -sphere by the centres of the given spheres, i.e., it is the angle between the surface elements which the k -sphere has in common with the two given spheres.

6. The non-oriented Sphere in the Geometry G_k .

If we restrict ourselves to turbines of inner radius k , the representative point lies on π_k and is subject to transformations induced on this prime by the projective group of G_k in the ambient space S_{n+2} . The resulting geometry may be considered as a geometry of non-oriented spheres in S_n , since every k -turbine has a non-oriented Mobius sphere, and conversely from any non-oriented sphere we may obtain a k -turbine by associating with it a concentric inner sphere of radius k . The section Ω_k of Ω by π_k is an invariant variety,

the points on which correspond to spheres of radius k and such spheres are carried over into other spheres of radius k . They play the same part here as points do in ordinary Inversion Geometry. Unless otherwise stated, every sphere mentioned in this para is to be considered non-oriented.

The fundamental operation here is " k -inversion with respect to a given sphere S ". This is an involutonic transformation of k -spheres into k -spheres which interchanges the two k -spheres in any coaxial system of spheres of which S is a member. If a k -sphere is bisected by S , then it is its own transform in the k -inversion determined by S . If we take the k -sphere as the basic element of the geometry G_k , any sphere not of radius k may be regarded as the totality of k -spheres bisected by it. In this sense S is its own inverse in the k -inversion defined by it. On π_k , S is represented by a point s which is not on Ω_k since we suppose that S is not a k -sphere. The k -inversion $I_k(S)$ defined by S corresponds to the involutonic projective transformation of π_k which has s for fixed point and its polar variety with respect to Ω_k as fixed prime. The points on the section of this polar prime with Ω_k correspond to k -spheres bisected by S as may be seen from (4.4). More generally, two spheres of radii R_1, R_2 for which $d^2 = t_1^2 + t_2^2 = R_1^2 + R_2^2 - 2k^2$ correspond to points conjugate with respect to Ω_k since when they are converted into k -turbines we have $d = t_{12}$, $R_1^2 = k^2 + t_1^2$ and $R_2^2 = k^2 + t_2^2$. If p, q be two corresponding points in $I_k(S)$, the sections of Ω_k by their polar primes are carried over into each other. Thus

The inversion $I_k(S)$ replaces every k -sphere by the other k -sphere in the pencil of spheres determined by it and S . All the k -spheres which are bisected by a sphere P are carried over into k -spheres which are bisected by another sphere Q . P and Q are then transforms of each other in the k -inversion $I_k(S)$.

It is known that all projective transformations which carry a quadric into itself may be obtained by successive involutonic transformations of the type discussed above. Thus the k -inversion is the basic operator which generates the group G_k .

7 Principle of Transference from G_0 to G_k .

Given any theorem in Mobius geometry G_0 , we may express it as a projective relation between a set of points on the prime $\pi_0 = x_{n+1} = 0$ and the section Ω_0 of Ω by π_0 . Any projective transformation between π_0 and π_k which carries Ω_0 into Ω_k will give a configuration with the same projective relationship to Ω_k as the original system had to Ω_0 . Interpreting these relations in terms of the concepts of G_k we have a dual theorem in G_k for every theorem in G_0 . All that is necessary is a scheme of interpretation

like the one given below of projective relations in π_k in terms of the concepts of G_k

(All the spheres referred to in this table are non oriented)

Situation in a Projective S_{n+1} with an invariant quadric ω	Interpretation in G_0 $S_{n+1} \equiv \pi_0, \omega \equiv \Omega_0$	Interpretation in G_k $S_{n+1} \equiv \pi_k, \omega \equiv \Omega_k$
Point	Sphere	Sphere
Point on the quadric	Sphere of radius zero	Sphere of radius k
Projective separation of two points p, q with respect to the quadric ω as absolute	Angle of intersection of the two spheres P and Q	The angle between the two diametral sections of a k sphere bisected by both P and Q
The tangent prime at p passes through q	The point P lies on the sphere Q	The k sphere P is bisected by Q
Two points p, q conjugate w r t the quadric	Two spheres P, Q which are mutually orthogonal	Two spheres of radii R_1, R_2 with their centres d apart where $d^2 = R_1^2 + R_2^2 - 2k^2$
Two points p, q whose join touches the quadric	The spheres P and Q touch	The common section of P and Q is a sphere (in a lower dimension) of radius k
Projective transformation of period 2 with p for invariant point and its polar prime w r t the quadric for fixed prime	Möbius Inversion	k inversion
The automorphic group of ω in S_{n+1}	Inversion group of sphere geometry in S_n	The group of the geometry G_k

As an example of such generalisation let us take the configuration formed by two Hart-tetrads of circles. We have the result³ —

It is possible to find two tetrads of circles in a plane such that each circle of one system has with each circle of the other system a chord of the same length k

In the same manner if the Miquel-Clifford configuration be considered as one in inversion Geometry, and generalised into a result in G_k , we have the following chain of theorems⁴

Take two circles C_1, C_2 which bisect a k -circle (circle of radius k) named C . There is then another k -circle C_{12} (or C_{21}) which is also bisected by them.

³ Vide my paper, "On a principle of duality in circle sphere and line Geometries," *Mathematische Zeitschrift*, Bd 44, Heft 2, p 194

⁴ A different generalisation of the Miquel-Clifford configuration is given in the paper referred to in the previous footnote (vide page 187).

If we take three circles C_1, C_2, C_3 which bisect a k -circle C , the three k -circles C_{12}, C_{23}, C_{31} are all bisected by a circle C_{123}

Taking four circles C_1, C_2, C_3, C_4 all of which bisect the k -circle C the four circles $C_{123}, C_{234}, C_{341}, C_{412}$ obtained by the process mentioned above all bisect a k -circle C_{1234} and so on

a k -circle being associated with an even number, and a circle of different radius with an odd number of circles C_r

When $k = 0$ we have the classical Miquel-Clifford configuration

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DYES DERIVED FROM CHRYSOQUINONE.

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AND

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Received May 30, 1938

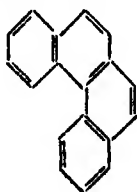
(Communicated by Sir C V Raman, Kt, FRS NI)

UNTIL before the War, the hydrocarbon phenanthrene which is present in anthracene oil or green oil to the extent of about 30 per cent, and which is so interesting from the theoretical point of view, was almost a waste product and was scarcely manufactured in the pure state. In 1916, Mukherjee and Watson¹ prepared an interesting series of vat and other dyestuffs from phenanthraquinone. The work was continued by Watson and Dutt,² Sircar and Dutt³ and Dutt,⁴ and phenanthraquinone was shown to be capable of yielding quite an interesting array of colouring matters of great technical value, and some of these are actually being manufactured.

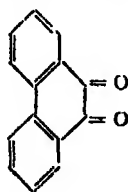
Chrysene or naphthphenanthrene is another hydrocarbon of coal tar obtained from the higher boiling fractions, which has not found any technical application as yet, and as such, it has still remained of purely theoretical interest. Structurally, the two hydrocarbons phenanthrene (I) and chrysene (II) and their oxidation products, phenanthraquinone (III) and chrysoquinone (IV) are so closely alike, that it is quite natural to expect that chrysene



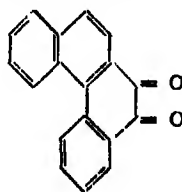
(I)



(II)



(III)



(IV)

would yield dyestuffs closely analogous to phenanthrene. This was supported by the observations of the present authors that chrysoquinone dyes wool and cotton from an alkaline hydrosulphite vat to beautiful orange shades. The present investigation was therefore undertaken with the object of preparing colouring matters from chrysene *via* chrysoquinone. The attempts were divided into three parts

A Attempts to Prepare New Hydroxy Derivatives

It has been shown by Mukherjee and Watson¹ that the introduction of hydroxy groups into the molecule of phenanthraquinone even by methods of great value in the case of anthraquinone dyestuffs, namely by the action of fuming sulphuric acid and boron trioxide and also by concentrated sulphuric acid and manganese dioxide, was impossible on account of the ease with which the molecule was destroyed by oxidation by these reagents. Similar difficulties were met with in the case of chrysoquinone, and therefore, it was thought advisable to prepare the hydroxy derivatives through nitration, reduction and subsequent diazotisation followed by hydrolysis.

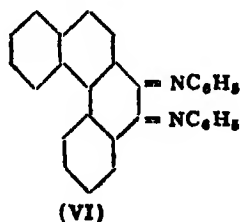
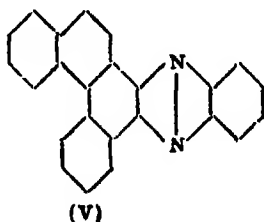
The nitration was successful, but the amines could not be obtained in any yield by reduction, as during the process of reduction with a metal and acid, the amines formed metallic complexes which were quite insoluble in water and consequently could not be satisfactorily decomposed with hydrogen sulphide.

B Attempts to Prepare Anilino Derivatives of Chrysoquinone

On account of serious difficulties in the methods to produce amino-derivatives from chrysoquinone, the possibilities of dyes in the form of hydroxy-chrysoquinones or acylamino-chrysoquinones were out of question. Consequently the bromination of chrysoquinone with formation of mono- and polybromo derivatives was the only practicable first step towards the production of anilino-chrysoquinones. It was possible to prepare three bromo derivatives of chrysoquinone, two of which were isomeric monobromo derivatives and the third was a pentabromo derivative. From these three bromo derivatives, three anilino derivatives were subsequently obtained, two of which were isomeric monoanilino derivatives and the third was a tetraanilino-monobromo derivative. These have got interesting dyeing properties and dye wool in violet shades.

C Attempts to Prepare Condensation Products of Chrysoquinone with Aromatic Amines

Chrysoquinone condenses fairly easily with aromatic amines with formation of chrysophenazines (V) and chrysoquinone-anilides (VI) and condensation



products were obtained with the following amines *o*-phenylene-diamine, *o*-aminophenol, 1 2-naphthalenediamine, *o*-anisidine, *o*-toluidine, *m*-toluidine, α -naphthylamine, β -naphthylamine, *o*-phenetidine, *p*-phenetidine, aniline, phenylhydrazine and 2 3-diamino-phenazine The behaviour of all the azines and anilides obtained in this way was normal All these compounds on examination were found to be good dyestuffs They dye unmordanted wool from an acid-bath, and also cotton from hydrosulphite vat in various shades ranging from brilliant yellow to dark violet Their absorption maxima range from 4,400 to 5,900 in Angstrom units

Experimental

Preparation of chrysoquinone —The best oxidising agent for the preparation of chrysoquinone was found to be sodium dichromate in glacial acetic acid Finely powdered chrysene (5 gm) was added to a solution of sodium dichromate (22 gm) in glacial acetic acid (50 c c) and the mixture refluxed on a sand-bath for nine hours An equal volume of hot water was then added and the crystalline precipitate of chrysoquinone filtered off and recrystallised from boiling glacial acetic acid Orange-red glistening plates, melting at 239° C Yield, 4.75 gm

Mononitro-chrysoquinone —Chrysoquinone (1 gm) was dissolved in concentrated nitric acid (S.G. 1.4, 10 c c) and the solution allowed to stand for 24 hours The mixture on dilution with water yielded the nitro-derivative as a yellow precipitate, which was crystallised from nitrobenzene in glistening yellow needles, melting at 256–57° C (Found N = 4.85, $C_{18}H_9O_4N$ requires N = 4.62 per cent)

Dinitro-chrysoquinone —Chrysoquinone (1 gm) was heated with concentrated nitric acid (10 c c) on a water-bath under reflux for three hours On cooling the solution, the dinitro derivative separated out in orange-yellow crystals The product was recrystallised from nitrobenzene in fine yellow prisms melting at 235° C Yield, 0.75 gm (Found N = 8.81, $C_{18}H_7O_6N_2$ requires N = 8.59 per cent)

Tetranitro-chrysoquinone —Chrysoquinone (1 gm) was treated with fuming nitric acid (S.G. 1.51, 10 c c) and the resultant solution heated on the water-bath under reflux for eight hours On cooling the tetranitro derivative separated as an orange microcrystalline powder The substance is insoluble in all the organic solvents It can only be recrystallised from fuming nitric acid in microscopic prisms, melting above 300° C Yield, 1.21 gm. (Found N = 12.5, $C_{18}H_5O_{10}N_4$ requires N = 12.78 per cent)

Monobromo-chrysoquinone (A) —Chrysoquinone was dissolved in nitrobenzene (1 gm in 20 c c) and the solution treated with bromine (1 c c) in

the same solvent (10 c c) The mixture was heated on an oil-bath under reflux at 110°C for two hours On cooling the monobromo compound crystallised out in yellow glistening leaflets melting at 246°C (Found $\text{Br} = 24.1$, $\text{C}_{18}\text{H}_9\text{BrO}_2$ requires $\text{Br} = 23.7$ per cent)

Monobromo-chrysoquinone (B)—This substance was prepared in the same manner as the above-mentioned compound with the exception that glacial acetic acid was used as the solvent instead of nitrobenzene The substance crystallised from glacial acetic acid in glistening yellow needles melting at 218°C (Found $\text{Br} = 24.08$, $\text{C}_{18}\text{H}_9\text{BrO}_2$ requires $\text{Br} = 23.7$ per cent)

Pentabromo-chrysoquinone—Chrysoquinone (1 gm) was heated with a large excess of bromine (5 c c) in a sealed tube under pressure at 100°C for six hours The product was crystallised from nitrobenzene in glistening orange-yellow leaflets melting above 300°C (Found $\text{Br} = 64.8$, $\text{C}_{18}\text{H}_5\text{Br}_5\text{O}_2$ requires $\text{Br} = 64.3$ per cent)

Monoanilino-chrysoquinone (A)—This was obtained from monobromo-chrysoquinone (A) by treatment with aniline in presence of copper-bronze according to the well-known method of Ullmann The anilino compound was crystallised from a mixture of nitrobenzene (1 part) and glacial acetic acid in dark brown microscopic needles melting at $210\text{--}12^{\circ}\text{C}$ (Found $\text{N} = 4.17$, $\text{C}_{24}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{N} = 4.01$ per cent)

Monoanilino-chrysoquinone (B)—This was prepared from monobromo-chrysoquinone (B) in the same way as the above-mentioned compound It could not be crystallised, but was purified from alcohol The substance is a dark green powder melting at $153\text{--}55^{\circ}\text{C}$ (Found $\text{N} = 4.47$, $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{N} = 4.01$ per cent)

Tetranilino-bromo-chrysoquinone—This was obtained from pentabromo-chrysoquinone by Ullmann's reaction with aniline in the usual manner. It could not be crystallised, but was purified by solution in nitrobenzene and precipitation with alcohol It is a dark brown powder melting at $291\text{--}93^{\circ}\text{C}$ (Found $\text{N} = 47$, $\text{C}_{42}\text{H}_{25}\text{O}_2\text{N}_4\text{Br}$ requires $\text{N} = 7.98$ per cent)

Chrysophenazine—This was obtained by condensation of chrysoquinone with *o*-phenylene diamine in molecular proportions in boiling glacial acetic acid solution It crystallised from nitrobenzene in glistening yellow needles melting at $207\text{--}08^{\circ}\text{C}$ and from glacial acetic acid in bright yellow prisms melting at 199°C (Found $\text{N} = 8.08$, $\text{C}_{24}\text{H}_{14}\text{N}_2$ requires $\text{N} = 8.48$ per cent)

Chryso-1 2-naphthazine—This was obtained in a similar way to the above, by using 1 2-naphthalene-diamine in place of *o*-phenylenediamine

It crystallised from boiling toluene in bright yellow needles with a silky lustre M P 238°C (Found $\text{N} = 7.23$, $\text{C}_{30}\text{H}_{16}\text{N}_2$ requires $\text{N} = 7.36$ per cent)

Chrysophenoxazine—This was obtained by condensation of chrysoquinone (1 mol) with *o*-aminophenol (2 mols) in hot glacial acetic acid solution. The dark brown precipitate obtained by pouring the reaction product into water was crystallised from alcohol in brown microscopic needles melting at 236°C (Found $\text{N} = 6.5$, $\text{C}_{30}\text{H}_{20}\text{O}_2\text{N}_2$ requires $\text{N} = 6.8$ per cent)

Chrysoquinone-di-anilide—This was obtained by the condensation of chrysoquinone with excess of aniline in glacial acetic acid solution. The reaction product was poured into dilute hydrochloric acid and the precipitated compound crystallised from a mixture of equal parts of nitrobenzene and alcohol in dark brown microscopic needles melting at $228\text{--}29^{\circ}\text{C}$ (Found $\text{N} = 6.42$, $\text{C}_{30}\text{H}_{20}\text{N}_2$ requires $\text{N} = 6.86$ per cent)

Chrysoquinone-di-o-toluidide—This was obtained from chrysoquinone and *o*-toluidine in a similar way to the above. Brown needles melting above 300°C (Found $\text{N} = 6.6$, $\text{C}_{32}\text{H}_{24}\text{N}_2$ requires $\text{N} = 6.4$ per cent)

Chrysoquinone-di-m-toluidide—Obtained from chrysoquinone and *m*-toluidine as above. Brown needles melting at $163\text{--}65^{\circ}\text{C}$ (Found $\text{N} = 6.24$, $\text{C}_{32}\text{H}_{24}\text{N}_2$ requires $\text{N} = 6.4$ per cent)

Chrysoquinone-di-o-amsidine—This was obtained by condensing chrysoquinone with excess of *o*-amsidine in boiling glacial acetic acid solution. After refluxing for three hours, the product was poured into dilute hydrochloric acid, and the precipitate crystallised from a mixture of equal parts of nitrobenzene and glacial acetic acid in dark brown needles M P $160\text{--}63^{\circ}\text{C}$ (Found $\text{N} = 5.92$, $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_2$ requires $\text{N} = 5.65$ per cent)

Chrysoquinone-di-o-phenetidine—Chrysoquinone (2 gm) was directly condensed with *o*-phenetidine (5 gm) by heating under reflux for three hours. The product was poured into dilute hydrochloric acid and the precipitated compound crystallised from alcohol M P $188\text{--}90^{\circ}\text{C}$ (Found $\text{N} = 5.44$, $\text{C}_{34}\text{H}_{28}\text{O}_2\text{N}_2$ requires $\text{N} = 5.6$ per cent)

Chrysoquinone-di-p-phenetidine—This was obtained from chrysoquinone and *p*-phenetidine in the same way as above M P $205\text{--}07^{\circ}\text{C}$ (Found $\text{N} = 5.56$, $\text{C}_{34}\text{H}_{28}\text{O}_2\text{N}_2$ requires $\text{N} = 5.6$ per cent)

Chrysoquinone-di- α -naphthylamide—This was obtained from chrysoquinone and α -naphthylamine by condensation in hot glacial acetic acid solution, in the usual manner. The product crystallised from a mixture of equal volumes of nitrobenzene and glacial acetic acid in dark brown

needles melting at 198–200° C (Found N = 5.32, $C_{38}H_{24}N_2$ requires N = 5.47 per cent)

Chrysoquinone-di-β-naphthylimide—This was obtained from chrysoquinone and β-naphthylamine in the same way as the above M P 203° C (Found N = 5.83, $C_{38}H_{24}N_2$ requires N = 5.47 per cent)

Properties of the Chrysoquinone Dyestuffs

Name of the compound (c q = chrysoquinone)	Shade of dyeing on wool from acid-bath	Shade of dyeing on cotton from hydro- sulphite vat	Absorption maxima in wave lengths
Chrysoquinone	Light yellow	Orange yellow	4400
Mononitro-c q		Light orange	4400
Dinitro-c q	..	Light brown	4560
Tetranitro-c q	.	Light brown	Insoluble
Monobromo-c q (A)		Light yellow	4350
Monobromo-c q (B)	..	Light yellow	4400
Monoanilino-c q (A)	Dark neutral grey	Dark grey	5850
Monoanilino-c q (B)	Dark reddish-violet	Brownish-violet	5900
Tetranilinobromo-c q		Bottle green	Insoluble
Chrysophenazine	Greenish-yellow	Greenish-yellow	4350
Chrysonaphthazine	Greenish-yellow	Greenish-yellow	4350
Chrysophenoxazine	Orange-yellow	Orange-yellow	4350
C q -dianilide	Medium yellow		4850
C q -di-o-toluidide	Medium yellow (broken tones)	.	4970
C q -di-m-toluidide	Dark neutral-grey		4900
C q -di-anisidide	Medium grey		5870
C q -di-o-phenetidide	Dark neutral-grey	.	5900
C q -di-p-phenetidide	Greyish-yellow		Insoluble
Chryso-2,3-diamido- phenazincazine	Dark reddish-violet		5050
C q -di-α-naphthylimide	Dark violet-red		5270
C q -di-β-naphthylimide	Light violet		5100
C q -di-phenylhydrazone	Dark brown	.	5150

Chrysoquinone-diphenylhydrazone—This was obtained from chrysoquinone and excess of phenylhydrazine in glacial acetic acid solution, in the usual manner. It crystallised from a mixture of equal parts of nitrobenzene and glacial acetic acid in dark brown microscopic needles melting at 228–29° C (Found N = 12.65, $C_{20}H_{12}N_4$ requires N = 12.78 per cent.)

Chryso-2,3-diamidophenazineazine—This was obtained from chrysoquinone and 2,3-diamidophenazine by condensation in glacial acetic acid solution. The substance was crystallised from nitrobenzene in almost black needles melting above 300° C (Found N = 12.8, $C_{20}H_{12}N_4$ requires N = 12.9 per cent.)

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- 2 Watson and Dutt, *ibid*, 1921, 119, 1211
- 3 Sircar and Dutt, *ibid*, 1922, 121, 1944
- 4 Dutt, *ibid*, 1922, 121, 1951

STUDIES IN THE FRIEDEL-CRAFTS REACTION.

Part IV. The Action of Acetyl Chloride and Acetic Anhydride on Resorcinol and its Derivatives An Evidence for γ -Substitution in the Resorcinol Nucleus

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PHENOLIC ethers have been condensed with acetyl chloride and acetic anhydride in the presence of anhydrous aluminum chloride with the formation of methoxy-acetophenones which, on demethylation, give their hydroxy-derivatives. The literature is very scanty with regard to the use of free phenols in such condensations. As we required O-hydroxy-acetophenones and their substitution products for the coumarin as well as the chromone synthesis, we thought that the best method would be the application of the Friedel-Crafts Reaction to the free phenols themselves. The Nencki Reaction¹ which usually gives this type of ketones does not give a good yield when higher fatty acids or aromatic acids are used.

An additional point of interest attaches itself to the use of resorcinol and its derivatives in this type of condensation from the view-point of substitution. Resorcinol (or 1,3-dihydroxy-benzene) undergoes monosubstitution at position 4 (β -substitution) and not at position 2 (γ -substitution) because the former position receives a greater amount of electron-accession from the two hydroxyl groups than the latter. The second substituent takes up again position 6 (β -position) and not position 2, which is attacked only when positions 4 and 6 are occupied. Baker and co-workers² have brought forward some evidence of γ -substitution in the case of certain derivatives of resacetophenone, and our object has been to see whether γ -substitution would take place in the case of resorcinol or its monosubstitution derivatives. With this object in view, we have condensed resorcinol, 4-ethylresorcinol, β -methylresorcyate, resacetophenone (4-acetylresorcinol) and orcinol with either acetyl chloride or acetic anhydride with the following results —

Resorcinol and acetyl chloride gave 4-acetyl resorcinol unaccompanied by any trace of 2-acetylresorcin. Similarly 4-ethylresorcinol yielded 2,4-dihydroxy-5-ethylacetophenone, not a trace of the isomeric 2,6-dihydroxy-3-ethylacetophenone being formed. An authentic specimen of the latter ketone

was synthesised from methyl 2 4-dihydroxy-5-ethylbenzoate and acetyl chloride in the presence of anhydrous aluminium chloride, hydrolysing the resulting ester, and decarboxylating the corresponding acid. The same ketone was also obtained from Shah and Samant's³ 7-hydroxy-6-ethyl-4-methyl coumarin by Limaye's process.⁴ Incidentally we have studied some of the properties of 8-acetyl-7-hydroxy-6-ethyl-4-methyl coumarin, *e.g.*, the preparation of functional derivatives, bromination and hydrolysis of the bromocoumarin.

β -Methylresorcyate did not condense with acetyl chloride at the ordinary temperature, but acetic anhydride at 100° gave methyl 2 4-dihydroxy-5-acetyl benzoate unaccompanied by any detectable trace of the isomeric methyl 2 4-dihydroxy-3-acetyl benzoate. The constitution of the ester was proved by following the method of Liebermann and Lindemann.⁵

Resacetophenone and acetic anhydride gave an equimolecular mixture of 2 4-diacetyl- and 4 6-diacetylresorcinols. Orcinol reacted with acetyl chloride giving mainly resacetophenone (2 4-dihydroxy-6-methylacetophenone) to gather with a small amount of 5-hydroxy-4 7-dimethyl coumarin which could arise only from the isomeric 2 6-dihydroxy-4-methyl-acetophenone, by the acetylation of one of the hydroxyl groups and subsequent ring-closure.

Thus we conclude from our experiments that resacetophenone and orcinol are the only two resorcinol derivatives which undergo γ -substitution side by side with the normal reaction (β -substitution). Baker (*loc cit.*), while studying the intramolecular rearrangements of certain resacetophenone derivatives, has made similar observations. Instances of γ -substitution in the case of orcinol exist in literature. Thus it undergoes the Pechmann Reaction with open-chain as well as cyclic β -ketonic esters giving 5-hydroxy-coumarins as observed by Dey⁶, and Ahmad and Desai,⁷ though malic acid gives the 7-hydroxy-coumarin. By condensing orcinol with glacial acetic acid in the presence of phosphorus oxychloride, Rasinski⁸ obtained a ketone which was proved to be 2 6-dihydroxy-4-methyl-acetophenone by Ludwinowsky and Tambor.⁹ Recently Shah and his co-workers¹⁰ have brought forward the evidence of γ -substitution in resorcinol derivatives, in course of studying Pechmann and Gattermann Reactions. We are busy extending these observations to β -resorcyaldehyde, 4-nitroresorcinol, 4-cyanoresorcinol and orcinol derivatives.

Experimental

Condensation of acetyl chloride with resorcinol —

A mixture of resorcinol (5.9 g), acetyl chloride (3.3 c.c.), anhydrous aluminium chloride (6.9 g) and nitrobenzene (50 c.c.) was kept at the ordinary

temperature for 24 hours. After decomposing aluminium chloride with dilute ice-cold hydrochloric acid, the nitrobenzene was removed in steam and the precipitate obtained on cooling was collected, dried and crystallised from benzene, when colourless needles melting at 146° were obtained. This was identified as resacetophenone by mixed m.p. with an authentic specimen prepared by Nancki's method (yield 65 per cent). The aqueous mother-liquor was saturated with salt, and extracted with ether. The gummy residue, on purification through the alkali treatment gave only resacetophenone, and no detectable trace of 2-acetylresorcinol. 4-Ethylresorcinol, on similar condensation with acetyl chloride, gave 2,4-dihydroxy-5-ethylacetophenone,¹¹ and not a trace of the isomeric 2,6-dihydroxy-3-ethylacetophenone, which was synthesised as follows.

Synthesis of 2,6-dihydroxy-3-ethylacetophenone —

(A) A solution of methyl 2,4-dihydroxy-5-ethylbenzoate (2 g) and acetic anhydride (1.2 c.c.) in dry nitrobenzene (10 c.c.) was added to the solution of anhydrous aluminium chloride (3.6 g) in nitrobenzene (30 c.c.) with cautious cooling, and the mixture heated in an oil-bath at 110° for two hours. Excess of aluminium chloride was decomposed by dilute, ice-cold hydrochloric acid, and the nitrobenzene steam distilled off. The solid obtained on cooling crystallised from dilute alcohol in colourless needles melting at 76° (Found C, 60.4, H, 6.1, $C_{13}H_{14}O_5$ requires C, 60.5, H, 5.9 per cent).

Methyl 2,4-dihydroxy-3-acetyl-5-ethylbenzoate is volatile in steam, and is slightly soluble in petrol and hexane, but very easily soluble in benzene, acetic acid, acetone, and alcohol. Its alcoholic solution gave a dark-violet colouration with aqueous ferric chloride.

Hydrolysis of the above ester with caustic soda to 2,6-dihydroxy-3-ethylacetophenone — A solution of the ester (1 g) in 10 per cent caustic soda (10 c.c.) was heated on sand-bath, for two hours, and acidified with dilute hydrochloric acid on cooling. The precipitated solid was treated with cold sodium bicarbonate solution and the residue crystallised from dilute alcohol when yellowish needles melting at 135° were obtained (found C, 66.4, H, 6.8, $C_{16}H_{18}O_5$ requires C, 66.6, H, 6.6 per cent). More of the same ketone was obtained on extracting with ether, the acid mother-liquor saturated with sodium chloride. The alcoholic solution of the ketone gave green colouration with ferric chloride, while it dissolved in concentrated sulphuric acid with a yellow colour.

The semicarbazone, prepared in the usual manner, crystallised from alcohol in needles melting at 252° (Found C, 55.3, H, 6.4, $C_{11}H_{13}O_2N_3$ requires C, 55.7, H, 6.3 per cent). On condensing this ketone with acetic

anhydride in the usual manner, 2 6-diacyl-4-ethylresorcinol was easily obtained, and this crystallised from dilute alcohol in fine, colourless needles melting at 76°. This was appreciably volatile in steam, and was fairly soluble in petrol, and hexane. Its alcoholic solution gave dark reddish-brown colouration with aqueous ferric chloride (Found C, 64.6, H, 6.2, $C_{12}H_{14}O_4$ requires C, 64.9, H, 6.3 per cent)

The semicarbozone crystallised from alcohol in pale-yellow needles melting at 267°

(B) Preparation of 6-ethyl-7-hydroxy-4-methyl coumarin—A mixture of ethylresorcinol (10 g), acetoacetic ester (10 g) and 73 per cent sulphuric acid (50 c.c.) was left for 24 hours at the ordinary temperature, and poured over ice. The crude solid melted at 208°, but on crystallising it from alcohol, white needles melting at 213° were obtained (yield 80–85 per cent). This coumarin has been prepared by Shah and Samant, and also Chakravarty (*loc cit*). The methyl ether, prepared by the usual method, crystallised from dilute alcohol in colourless needles melting at 160° (Found C, 71.2, H, 6.6, $C_{13}H_{14}O_3$ requires C, 71.6, H, 6.4 per cent). The carboethoxy derivative was obtained by gradually treating the solution of the coumarin (0.2 g) in 10% caustic soda (5 c.c.) with ethyl chlorocarbonate (2 c.c.). The precipitated solid, after trituration with alkali, crystallised from dilute alcohol in colourless needles melting at 144° (Found C, 64.9, H, 6.0, $C_{15}H_{16}O_3$ requires C, 65.2, H, 5.8 per cent)

Attempts to bring about the Fries Transformation of the carboethoxy derivative by using either anhydrous aluminium chloride or zinc chloride were not successful

The acetyl derivative crystallised from dilute alcohol in prismatic needles melting at 143° (Found C, 68.1, H, 5.9, $C_{14}H_{14}O_4$ requires C, 68.3, H, 5.7 per cent)

Synthesis of 8-acetyl-7-hydroxy-6-ethyl-4-methylcoumarin—An intimate mixture of 7-acetoxy-6-ethyl-4-methylcoumarin (10 g) and finely powdered anhydrous aluminium chloride (25 g) was heated in an oil-bath at 140–50 for one hour. After decomposing the aluminium chloride with ice-cold hydrochloric acid, the solid was dissolved in sodium carbonate solution, and acidified with concentrated hydrochloric acid. The coumarin crystallised from dilute alcohol in straw-coloured needles melting at 139°. The alcoholic mother-liquor on evaporation left a residue (m.p. 105–10°), which was treated with benzene to dissolve the coumarin m.p. 139°. The benzene-insoluble portion proved to be the original 7-hydroxy-6-ethyl-4-methylcoumarin (yield 90 per cent). (Found C, 68.4, H, 6.0, $C_{14}H_{14}O_4$ requires

C, 68.3, H, 5.7 per cent) It dissolved in alkali with a yellow colour, and its alcoholic solution gave blackish-violet colour with ferric chloride. It did not give the acetyl, methyl and carboethoxy derivatives by the usual methods.

The semicarbazone did not melt upto 290° .

The Kostanecki Reaction with 4-methyl-6-ethyl-7-hydroxy-8-acetyl coumarin and synthesis of 4,2'-dimethyl-6'-ethyl-3-acetyl-coumarino (7,8)- γ -pyrone—The mixture of the coumarin (1 g), acetic anhydride (7 c.c.) and anhydrous sodium acetate (2.5 g) was heated in an oil-bath at $175-80^{\circ}$ for ten hours. The solid obtained by decomposing the mixture with water was filtered off and treated with 5 per cent NaOH solution to remove the unchanged coumarin. The coumarino- γ -pyrone crystallised from benzene in colourless needles melting at 192° . Its alcoholic solution did not give any colour with FeCl_3 solution. It dissolved in sodium hydroxide solution on warming, while its solution in concentrated sulphuric acid was yellow. (Found C, 69.0, H, 5.0, $\text{C}_{18}\text{H}_{16}\text{O}_6$ requires C, 69.2, H, 5.1 per cent.)

Hydrolysis of 4-methyl-6-ethyl-7-hydroxy-8-acetyl coumarin with 2N-NaOH—A solution of the coumarin (1 g) in 2N-caustic soda (15 c.c.) was heated on sand-bath under reflux for three hours, and the cooled solution was acidified with dilute hydrochloric acid. The filtered solid was shaken up with 2 per cent sodium bicarbonate solution, and the residue crystallised from alcohol, when yellowish needles melting at 135° were obtained. This hydroxy ketone was identical with the one prepared by hydrolysing the condensation product of methyl 2,4-dihydroxy-5-ethylbenzoate with acetic anhydride. On condensing it with acetoacetic ester in the presence of conc. H_2SO_4 , the coumarin (m.p. 139°) was obtained.

Bromination of 4-methyl-6-ethyl-7-hydroxy-8-acetyl-coumarin to 3-bromo-4-methyl-6-ethyl-7-hydroxy-8-acetyl-coumarin—The solution of the coumarin (2 g) in glacial acetic acid (25 c.c.) was gradually treated with a solution of bromine (2.5 c.c.) in glacial acetic acid (10 c.c.). The mixture which became warm immediately, was exposed to bright sunlight for one hour, and the crystalline solid that had separated out was filtered off. The crude solid (m.p. 176°) crystallised from dilute acetic acid in colourless needles melting at 180° . The glacial acetic acid mother-liquor, on dilution with water, gave a further amount of the bromo-compound contaminated with the original product. (Found Br, 24.8, $\text{C}_{14}\text{H}_{12}\text{O}_4\text{Br}$ requires Br, 24.6 per cent.)

Hydrolysis of the bromo-coumarin by sodium carbonate solution—A solution of the bromo-coumarin (2 g) in 5 per cent sodium carbonate solution (35 c.c.) was heated on sand-bath under reflux for two hours, cooled and extracted with ether. The ethereal solution gave, on the removal of the

solvent, a solid which crystallised from methyl alcohol in yellowish needles melting at 66° . This was 3-methyl-5-ethyl-6-hydroxy-7-acetyl-coumarone, because it was also obtained by the decarboxylation of the coumarilic acid described below (Found C, 71.4, H, 6.5, $C_{15}H_{14}O_3$ requires C, 71.6, H, 6.4 per cent)

The coumarone was soluble in hot caustic soda. Its alcoholic solution gave green colouration with $FeCl_3$. It could not be methylated, acetylated or carboethoxylated by the usual methods.

The semicarbazone crystallised from alcohol in small plates unmelted below 290° (Found C, 60.7, H, 6.3, $C_{14}H_{17}O_3N_3$ requires C, 61.1, H, 6.2 per cent)

The sodium carbonate solution, on acidification with concentrated hydrochloric acid, gave a solid which dissolved almost completely in the cold 2 per cent sodium bicarbonate solution. On acidification of the filtered solution, 3-methyl-5-ethyl-6-hydroxy-7-acetyl-coumarilic acid melting at $204-06^{\circ}$ (decomp) was obtained. The acid could not be satisfactorily crystallised from any solvent (Found C, 63.8, H, 5.4, $C_{14}H_{14}O_6$ requires C, 64.1, H, 5.3 per cent)

Condensation of methyl- β -resorcyate with acetic anhydride—The condensation of methyl- β -resorcyate with acetyl chloride at the ordinary temperature did not take place appreciably. The following method using the acetic anhydride was found to give the best yield of methyl 2,4-dihydroxy-5-acetylbenzoate after a number of trial experiments.

A solution of anhydrous aluminium chloride (7 g) in nitrobenzene (60 c c) was added to the solution of methyl- β -resorcyate (4 g) and acetic anhydride (2.5 g) in nitrobenzene (20 c c) and the mixture was heated on water-bath for four hours. After decomposing the aluminium chloride with ice-cold dilute hydrochloric acid, the nitrobenzene was steam-distilled off, and the residue filtered off. On purification through alkali treatment, the crude solid melted at $108-12^{\circ}$. On refluxing with hexane, the hexane-soluble portion crystallised in colourless needles melting at 124° mixed melting point with anhydrous methyl- β -resorcyate m.p. 124° was $98-100^{\circ}$ (Found C, 56.8, H, 4.8, Calc. for $C_{10}H_{10}O_5$ C, 57.1, H, 4.9 per cent)

The hexane-insoluble portion was treated with warm benzene which dissolved a portion of the residue. The solid obtained on the removal of benzene melted at 256° , and was identical with 2,4-dihydroxy-5-acetylbenzoic acid described below.

Hydrolysis of the ester to the acid—A solution of the ester (1 g) in normal sodium hydroxide (10 c c) was heated on sand-bath under reflux for three

hours On acidification, the free acid which was identified as 2,4-dihydroxy-5-acetyl-benzoic acid crystallised from dilute alcohol in small needles melting at 256° On heating the acid in an oil-bath at 250°, much of the product sublimed, and the sublimate (m.p. 146°) was identified as resacetophenone by a mixed melting point (Liebermann and Lindemann (*loc cit*))

Condensation of resacetophenone with acetic anhydride—Resacetophenone did not condense with acetyl chloride at ordinary temperature The following conditions gave the best result with acetic anhydride

A solution of anhydrous aluminum chloride (16 g) in nitrobenzene (100 c.c.) was added to a mixture of resacetophenone (8 g), acetic anhydride (6 g) and nitrobenzene (35 c.c.), and the resulting mixture was heated in an oil-bath at 105–110° for two hours After decomposing the aluminum chloride, nitrobenzene was cautiously steam-distilled off (Care was taken to see that 2,4-diacetyl resorcinol does not volatilise away) The solid obtained on cooling was filtered off, and the mother-liquor was extracted with ether after saturating it with salt The solid residue was first boiled with 10 per cent NaOH, as it was sticky, and the solid recovered after acidification with concentrated hydrochloric acid The dry solid was first extracted with benzene in which most of it dissolved The benzene solution, on cooling, deposited 4,6-diacetylresorcinol melting at 185° (1.5 g) The benzene was removed from the mother-liquor, and the residue extracted with hexane The hexane solution, on cooling, deposited 2,4-diacetylresorcinol melting at 85–86° (1.5 g) Authentic specimens of 4,6-acetylresorcinol and 2,4-diacetyl resorcinol were prepared for comparison by following Baker's directions (*loc cit*)

Condensation of orcinol with acetyl chloride—Orcinol (6 g) dissolved in nitrobenzene (25 c.c.) was added to the solution of aluminium chloride (6.5 g) in nitrobenzene (50 c.c.) and finally acetyl chloride (5 g) was cautiously added After keeping the mixture for 24 hours, and decomposing the aluminium chloride with ice-cold hydrochloric acid, the nitrobenzene was steam-distilled off, and the solid filtered and dried A considerable portion went in solution in benzene leaving a small residue (0.5 g) melting at 230–235° On recrystallisation from dilute alcohol, it melted at 258° and was identified as 4,7-dimethyl-5-hydroxy-coumarin by comparison with an authentic specimen

The benzene solution, on concentration and cooling, deposited glistening plates melting at 159–160°, and was identified as orsacetophenone, by its properties (4 g) A small amount of orsacetophenone (0.5 g) was also recovered by extracting with ether the original mother-liquor

Summary

Acetyl chloride and acetic anhydride have been condensed with resorcinol 4-ethylresorcinol, methyl β -resorcyate, resacetophenone and orcinol in the presence of anhydrous aluminium chloride and it is found that resacetophenone and orcinol show evidence of γ -substitution side by side with usual β -substitution. Two independent methods of synthesising 2,6-dihydroxy-3-ethyl-acetophenone have been worked out, as this unknown ketone was required during the course of the work.

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DIOPHANTISCHE PROBLEME.

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I Das Gleichungssystem

$$\begin{cases} X_1 + X_2 + X_3 + X_4 + X_5 + X_6 + X_7 = 0 \\ X_1^3 + X_2^3 + X_3^3 + X_4^3 + X_5^3 + X_6^3 + X_7^3 = 0 \\ X_1^5 + X_2^5 + X_3^5 + X_4^5 + X_5^5 + X_6^5 + X_7^5 = 0 \end{cases} \text{ in ganzen rationalen Zahlen}$$

(a) Es seien a und b beliebige ganze Zahlen. Wir setzen nun

$$\begin{aligned} A &= a^5 + a^4b - 3a^3b^2 - 11a^2b^3 - 11ab^4 - 3b^5, \\ B &= 2a^4b + 2a^3b^2 - 8a^2b^3 - 8ab^4 - 2b^5, \\ C &= -a^4b - a^3b^2 - 2a^2b^3 - 3ab^4 - b^5, \\ D &= -a^5 - a^4b - 8a^3b^2 - 10a^2b^3 - 3ab^4 - 3b^5, \\ E &= -a^5 - 2a^4b + a^3b^2 - 2a^2b^3 - 5ab^4 - 2b^5, \\ F &= -a^4b - 4a^3b^2 - 7a^2b^3 - 4ab^4 - b^5, \\ G &= a^5 + 2a^4b - 2a^3b^2 - 11a^2b^3 - 8ab^4 - 2b^5, \\ H &= -a^5 - 2a^4b - 3a^3b^2 - 6ab^4 - 2b^5, \\ J &= a^4b + 2a^3b^2 - 7a^2b^3 - 10ab^4 - 3b^5, \\ K &= a^5 + 2a^4b - 3a^3b^2 - 12a^2b^3 - 9ab^4 - 2b^5, \\ L &= a^5 + a^4b - 2a^3b^2 - 6a^2b^3 - 4ab^4 - b^5, \\ M &= a^4b - a^3b^2 - 12a^2b^3 - 11ab^4 - 3b^5, \\ N &= -2a^4b - 4a^3b^2 - 6a^2b^3 - 6ab^4 - 2b^5, \\ P &= -a^5 - a^4b + a^3b^2 - 3a^2b^3 - 3ab^4 - b^5 \end{aligned}$$

(β) Nun gilt die Identität

$$\begin{cases} A + B + C + D + E + F + G = H + J + K + L + M + N + P \\ A^2 + B^2 + C^2 + D^2 + E^2 + F^2 + G^2 = H^2 + J^2 + K^2 + L^2 + M^2 + N^2 + P^2 \\ A^3 + B^3 + C^3 + D^3 + E^3 + F^3 + G^3 = H^3 + J^3 + K^3 + L^3 + M^3 + N^3 + P^3 \\ A^4 + B^4 + C^4 + D^4 + E^4 + F^4 + G^4 = H^4 + J^4 + K^4 + L^4 + M^4 + N^4 + P^4 \\ A^5 + B^5 + C^5 + D^5 + E^5 + F^5 + G^5 = H^5 + J^5 + K^5 + L^5 + M^5 + N^5 + P^5 \\ A^6 + B^6 + C^6 + D^6 + E^6 + F^6 + G^6 = H^6 + J^6 + K^6 + L^6 + M^6 + N^6 + P^6 \end{cases}$$

Setzt man nun $S = \frac{A+P}{2} = \frac{B+N}{2} = \frac{C+M}{2} = \frac{D+L}{2} = \frac{E+K}{2} = \frac{F+J}{2} = \frac{G+H}{2}$, dann bekommt man, wenn man $(S-A)^n + (S-B)^n + (S-C)^n + (S-D)^n + (S-E)^n + (S-F)^n + (S-G)^n = (S-H)^n + (S-J)^n + (S-K)^n + (S-L)^n + (S-M)^n + (S-N)^n + (S-P)^n$ für $n = 1, 2, 3, 4, 5, 6$ setzt und wenn man die Glieder nach der Größe ordnet, Relationen von der Form

$$(\gamma) \quad X_1^n + X_2^n + X_3^n + (-X_4)^n + (-X_5)^n + (-X_6)^n + (-X_7)^n = X_1^n + X_2^n + X_3^n + X_4^n + (-X_5)^n + (-X_6)^n + (-X_7)^n \text{ für } n = 1, 3, 5$$

Daraus folgt

$$\begin{cases} X_1 + X_2 + X_3 + X_4 + X_5 + X_6 + X_7 = 0 \\ X_1^3 + X_2^3 + X_3^3 + X_4^3 + X_5^3 + X_6^3 + X_7^3 = 0 \\ X_1^5 + X_2^5 + X_3^5 + X_4^5 + X_5^5 + X_6^5 + X_7^5 = 0 \end{cases}$$

(Siehe "A. Moessner. Zahlentheoretische Untersuchungen" in *The Tohoku Mathematical Journal*, Vol 39, Part I!)

(δ) *Exempel* Setzt man $a = 3, b = 1$, so bekommt man die Identität $1^n + 109^n + 119^n + 363^n + 492^n + 640^n + 656^n = 24^n + 40^n + 188^n + 317^n + 561^n + 571^n + 679^n$ für $n = 1, 2, 3, 4, 5, 6$, wenn man zu jeder Base der gewonnenen Glieder die Zahl 453 addiert und dann die Glieder nach der Größe ordnet [also eine Identität, wie unter (β) gezeigt] NB — Die gleichmassige additive oder subtraktive Veränderung der Basen ist hier zulässig, denn gilt $A^n + B^n + C^n + D^n + E^n + F^n + G^n = H^n + J^n + K^n + L^n + M^n + N^n + P^n$ für $n = 1, 2, 3, 4, 5, 6$, dann gilt nach einem bekannten Satze der Zahlentheorie auch $(A \pm x)^n + (B \pm x)^n + (C \pm x)^n + (D \pm x)^n + (E \pm x)^n + (F \pm x)^n + (G \pm x)^n = (H \pm x)^n + (J \pm x)^n + (K \pm x)^n + (L \pm x)^n + (M \pm x)^n + (N \pm x)^n + (P \pm x)^n$ für $n = 1, 2, 3, 4, 5, 6$ bei beliebigem x

$$(\epsilon) \text{ Aus dem Exempel unter } (\delta) \text{ ergibt sich } S = \frac{1+679}{2} = \frac{109+571}{2} = \frac{119+561}{2} = \frac{363+317}{2} = \frac{492+188}{2} = \frac{640+40}{2} = \frac{656+24}{2} = 340$$

Man bekommt also $339^n + 231^n + 221^n = 23^n + 152^n + 300^n + 316^n$ für $n = 1, 3$ und 5

II Das Gleichungssystem

$$\begin{cases} A^3 + B^3 + C^3 = D^3 + E^3 + F^3 \\ A \cdot B \cdot C = D \cdot E \cdot F \end{cases}$$

Wir bekommen eine allgemeine Lösung dieses Systems, wenn wir setzen

$$\begin{aligned} A &= g [a (a^3 - b^3) x^3 - 2g (a^3 - b^3) xy + a (g^3 - a^3) y^3]; \\ B &= ad [(a^3 - b^3) x^3 - (g^3 - a^3) y^3], \end{aligned}$$

$$C = b [g (a^2 - b^2) x^2 - 2 a (g^2 - d^2) xy + g (g^2 - d^2) y^2],$$

$$D = d [a (a^2 - b^2) x^2 - 2 g (a^2 - b^2) xy + a (g^2 - d^2) y^2],$$

$$E = bg [(a^2 - b^2) x^2 - (g^2 - d^2) y^2],$$

$$F = a [g (a^2 - b^2) x^2 - 2 a (g^2 - d^2) xy + g (g^2 - d^2) y^2] \text{ mit beliebigen } g, a, b, d, x, y$$

Numerisches Exempel

Es ergibt $g = 1, a = 3, b = 2, x = 4, y = 1, d = 5$ die Lösung

$$\begin{cases} 16^2 + 195^2 + 158^2 = 80^2 + 26^2 + 237^2 \\ 16 \quad 195 \quad 158 = 80 \quad 26 \cdot 237 \end{cases}$$

III Das Gleichungssystem

$$\begin{cases} 4 & G^{2v} = K^4 + L^4 + M^4 + 2(x^2 + y^2 + z^2) \\ 4 & G^{4v} = K^8 + L^8 + M^8 + 2(x^4 + y^4 + z^4) \end{cases}$$

(1) Die Formel $2(i^2 + 3k^2)^v = (2ik + 3k^2 - i^2)^v + (2ik + i^2 - 3k^2)^v + (4ik)^v$ für $v = 2$ und 4 liefert Identitäten von der Form $2A^v = B^v + C^v + D^v$ für $v = 2, 4$ (cf. A. Moessner "General Formulæ for Constructing and solving certain simultaneous Equations" in *The Mathematics Student*, 1935, Vol. 3 I), wobei i und k beliebig sind

(2) Gilt $2A^v = B^v + C^v + D^v$ für $v = 2, 4$, dann gilt auch

$$\begin{cases} 2 & (A \cdot A')^2 = (B \cdot A')^2 + (C \cdot A')^2 + (D \cdot A')^2 \\ 2 & \cdot (A \cdot A')^4 = (B \cdot A')^4 + (C \cdot A')^4 + (D \cdot A')^4 \end{cases} \text{ für beliebiges } r$$

Wir setzen nun $\begin{cases} A \cdot A' = G'' \\ A \cdot A' = G'' \end{cases}, B \cdot A' = K, C \cdot A' = L \text{ und } D \cdot A' = M$

Dann geht die Gleichung über in

$$\begin{cases} 2 & G'' = K^2 + L^2 + M^2 \\ 2 & G''^2 = K^4 + L^4 + M^4 \end{cases} \text{ Diese Relation muss richtig bleiben, wenn man jede Seite quadriert, es muß also auch gelten}$$

$$(2 \cdot G'')^2 = (K^2 + L^2 + M^2)^2 \text{ und } (2 \cdot G''^2) = (K^4 + L^4 + M^4)^2$$

Wir bekommen

$$\begin{cases} 4 & G''^2 = K^4 + L^4 + M^4 + 2[(K \cdot L)^2 + (K \cdot M)^2 + (L \cdot M)^2], \\ 4 & G''^4 = K^8 + L^8 + M^8 + 2[(K \cdot L)^4 + (K \cdot M)^4 + (L \cdot M)^4] \end{cases}$$

Wir setzen hier $KL = x, KM = y, LM = z$ und haben die Lösung des vorgelegten Gleichungssystems

Numerisches Exempel $i = 1, k = 2$ ergibt die Relation $2 \cdot 13^v = 15^v + 7^v + 8^v$ für $v = 2, 4$ (NB! Da die Exponenten gerade sind, können negative Vorzeichen unberücksichtigt bleiben) $v = 3$ ergibt das Resultat

$$\begin{aligned} 2 \cdot (13 \cdot 13^3)^v &= (15 \cdot 13^3)^v + (7 \cdot 13^3)^v + (8 \cdot 13^3)^v \text{ für } v = 2, 4, \text{ also} \\ 2 \cdot (13^4)^v &= 32955^v + 15379^v + 17576^v \text{ für } v = 2, 4 \end{aligned}$$

Durch Quadrieren bekommt man

$$\begin{cases} 4 \cdot 13^{16} = 32955^4 + 15379^4 + 17576^4 + 2 [(32955 \cdot 15379)^2 + \\ \quad (32955 \cdot 17576)^2 + (15379 \cdot 17576)^2] \\ 4 \cdot 13^{20} = 32955^8 + 15379^8 + 17576^8 + 2 [(32955 \cdot 15379)^4 + \\ \quad (32955 \cdot 17576)^4 + (15379 \cdot 17576)^4] \end{cases}$$

IV Das Gleichungssystem

$$a + b + c = d + e + f$$

$$a^2 + b^2 + c^2 = d^2 + e^2 + f^2$$

$$a^3 + b^3 + c^3 = K^3$$

Wir setzen nach Euler

$$\begin{aligned} a &= (r + 3s)(r^2 + 3s^2) - 1, \quad b = -(r - 3s)(r^2 + 3s^2) + 1, \\ c &= -(r + 3s) + (r^2 + 3s^2)^2, \quad K = r - 3s - (r^2 + 3s^2)^2 \quad \text{Dann} \\ &\text{ist } a^3 + b^3 + c^3 = K^3 \end{aligned}$$

Nach einem Satze der Zahlentheorie gilt allgemein

$$\begin{aligned} A_1^n + A_2^n + A_3^n + \dots + A_x^n &= (p - A_1)^n + (p - A_2)^n + (p - A_3)^n \\ &+ \dots + (p - A_x)^n \quad \text{für } n = 1, 2, \text{ wenn } p = \frac{2}{x} (A_1 + A_2 + A_3 \\ &\quad + \dots + A_x) \text{ ist} \end{aligned}$$

Bei der vorgelegten Relation ist $x = 2$, also $p = \frac{2}{3} \cdot (a + b + c)$

Also gilt $a^n + b^n + c^n = (p - a)^n + (p - b)^n + (p - c)^n$ für $n = 1, 2$. Wir setzen $p - a = d$, $p - b = e$, $p - c = f$ und haben das vorgelegte System gelöst. Man bekommt immer ganzzahlige Lösungen, wenn man die Basen mit 3 multipliziert.

Numerisches Exempel $r = 2$, $s = 1$ ergibt $a = 34$, $b = 8$, $c = 44$; $K = 50$, gekürzt $17^3 + 4^3 + 22^3 = 25^3$. Um eine ganzzahlige Lösung zu bekommen, setzen wir $51^3 + 12^3 + 66^3 = 75^3 \cdot p = \frac{2}{3} (51 + 12 + 66) = 86$

Wir bekommen

$$\begin{cases} 51 + 12 + 66 = 35 + 74 + 20 \\ 51^3 + 12^3 + 66^3 = 35^3 + 74^3 + 20^3 \\ 51^3 + 12^3 + 66^3 = 75^3 \end{cases}$$

Exempel mit kleineren Zahlen

$$\begin{cases} 1 + 6 + 8 = 9 + 4 + 2 \\ 1^3 + 6^3 + 8^3 = 9^3 + 4^3 + 2^3 \\ 1^3 + 6^3 + 8^3 = 9^3 \end{cases}$$

V Die Gleichung $x^3 - 3y^3 = z^3$ in ganzen Zahlen

Wir setzen $y^3 = t$, dann bekommen wir $x^3 - 3t^3 = z^3$.

Für diese Gleichung besteht folgende Parameterlösung

$$x = m^3 + 9 mn^2 = m (m^2 + 9 n^2)$$

$$t = 3 m^2 n + 3 n^3 = 3 n (m^2 + n^2)$$

$$z = m^3 - 3 n^3 \quad \text{Dann bleibt noch zu lösen}$$

$$3 n (m^2 + n^2) = y^3$$

Hier sind folgende zwei Fälle zu unterscheiden

$$(\alpha) \begin{cases} m^2 + n^2 = 3 y'^3 \\ n = y''^3 \end{cases}$$

$$(\beta) \begin{cases} m^2 + n^2 = y'^3 \\ n = 3 y''^3 \end{cases}$$

Die Gleichung $m^2 + n^2 = 3 y'^3$ ist unmöglich, wie man leicht beweisen kann. Um das System (β) zu lösen, setzt man, $m = p^2 - q^2$ und $n = 2 pq$. Ausserdem müssen p und q Werte annehmen, die durch die nachfolgenden Gleichungspaare gegeben sind

$$(1) \quad p = 3 r^2 \quad q = 2 s^2$$

$$(2) \quad p = 2 r^2 \quad q = 3 s^2$$

$$(3) \quad p = 6 r^2 \quad q = s^2$$

$$(4) \quad p = r^2 \quad q = 6 s^2$$

Für den Fall (1) zum Beispiel findet man die Formeln

$$\begin{cases} x = (9 r^4 - 4 s^4) [(9 r^4 - 4 s^4)^2 + 81 (2 rs)^4] \\ y = 6 rs (9 r^4 + 4 s^4) \\ z = (9 r^4 - 4 s^4)^3 - 27 (2 rs)^4 \end{cases}$$

r und s sind beliebige ganze Zahlen

Der Leser stellt selbst leicht die Formeln für die anderen Fälle auf.

Exempel $r = 2, s = 1$ ergibt nach Vereinfachung $88235^3 - 3 \cdot 222^4 = 793^3$

VI Ganzzahlige Lösung zu $x^4 + y^3 = z^3$

Wir gehen aus von der Identität

$(m^3 - 3 mn^2)^3 + (3 m^2 n - n^3)^3 = (m^2 + n^2)^3$ Wir verwandeln nun den Ausdruck $m^3 - 3 mn^2 = m (m^2 - 3 n^2)$ in ein Quadrat, indem wir jeden Faktor dieses Produktes in ein Quadrat verwandeln, und wir gelangen so zu einer Identität, die eine unendliche Anzahl von Lösungen der vorgelegten Gleichung ergibt

$$[(r^2 + 3 s^2) (r^4 - 18 r^2 s^2 + 9 s^4)]^3 + [4 rs (r^2 - 3 s^2) (3 r^2 + 20 r^4 s^2 + 258 r^2 s^4 + 180 r^2 s^6 + 243 s^8)]^3 = (r^6 + 28 r^4 s^2 - 42 r^2 s^4 + 252 r^2 s^6 + 81 s^8)^3.$$

Exempel $r = 2, s = 1$ ergibt $329^4 + 57112^3 = 2465^3$

VII Ganzzahlige Lösung zu $x^4 + y^3 = z^6$

Wir gehen aus von $(m^3 + mn^2)^3 + (m^2 n + n^3)^3 = (m^2 + n^2)^3$ Wenn wir den Ausdruck $m^3 + mn^2 = m (m^2 + n^2)$ in ein Quadrat verwandeln wie unter VI,

so wird aus dem Kubus auf der 2 ten Gleichungsseite eine sechste Potenz
Nach Ausführung der Rechnungen ergibt sich die Identität

$$[(r^3 - s^3)(r^4 + 6r^2s^2 + s^4)]^3 + [4rs(r^3 + s^3)(r^4 + 6r^2s^2 + s^4)]^3 = (r^4 + 6r^2s^2 + s^4)^6$$

Exempel — $r = 2, s = 1$ ergibt $123^4 + 67240^3 = 41^6$

VIII Allgemeine ganzzahlige Lösung des Systems

$$\begin{cases} x^3 + xy + y^3 = z^3 & (1) \\ x + y = t^2 & (2) \end{cases}$$

Für die Gleichung (1) haben wir die Parameterlösung $x = m^3 - 3mn^2 - n^3, y = 3m^2n + 3mn^2 = 3mn(m + n), z = m^3 + mn + n^3$

Es bleibt aufzulösen $m^3 + 3m^2n - n^3 = t^3$

Man kennt eine Parameterlösung (2 Parameter) der allgemeineren Gleichung $m^3 + am^2n + bmn^2 + cn^3 = t^3$ (Siehe zum Beispiel Carmichael, *Analyse indéterminée*, 1929, Seite 58 und 59)

Durch Anwendung der bekannten Formeln wird gefunden

$$m = a^3 - 8p^3q - 12p^2$$

$$n = 4apq - 4p^2$$

a ist eine Funktion von p und q Hier der Ausdruck von a

$$a = -9p - 6pq - pq^2$$

$$t = a^3 + 6a^2p(q + 3) + 12ap^2(q + 2) + 8p^3(1 - 3q^2 - q^3)$$

Man kann t auch als Funktion von p und q allein darstellen

Exempel — $p = 1, q = 2, m = 597, n = -204$ ergibt

$$\begin{cases} x = 146731581 \\ y = -143588052 \\ z = 276237 \\ t = 1773 \end{cases}$$

DERIVATIVES OF SALICYLIC ACID.

Part XIII. Chlorosalicylic Acids and Their Methyl Ethers.

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3-SUBSTITUTED salicylic acids are difficult to obtain by direct substitution, the orienting influence is favourable to position 5. Chlorination¹ of salicylic acid has so far given a mixture consisting mainly of 5-chlorosalicylic acid, and small quantities of 3-chloro- and 3,5-dichlorosalicylic acids and chlorophenols, no conditions were known which would give each of these substances alone and separately. The methyl ethers of these acids had also not received proper attention, that of 3-chlorosalicylic acid being yet unknown, and those of 5-chloro- and 3,5-dichlorosalicylic acids² obtained indirectly from 2-methyl-4-chlorophenyl methyl ether and 2-methyl-4,6-dichlorophenyl methyl ether.

As the amides of these acids were required for some other work, convenient methods had to be worked out for the preparation of the above acids, which together with some new derivatives form the subject-matter of the present paper.

3-Chlorosalicylic acid—This acid has now been prepared in good yield by two different methods. Sulphonic acid group in 5-sulphosalicylic acid is unstable and can be substituted with hydrogen by superheated steam.³ This acid when chlorinated gave *3-chloro-5-sulphosalicylic acid* which on desulphonation at 160°–70° gave 3-chlorosalicylic acid.

In previous work with chloralsalicylamide, it has been found that the substitution of carboxyl group by chloralamide group changes the main orienting influence from position 5 to position 3. In agreement with this observation a good yield of *chloral-3-chlorosalicylamide* is obtained by the chlorina-

¹ Heubner and Brenken, *Ber.*, 1873, **6**, 174, Lassar-Cohn and Schultze, *ibid.*, 1905, **38**, 3300, Ullmann and Kopetschni, *ibid.*, 1911, **44**, 428.

² Paratoner and Condorelli, *Gaz.*, 1898, **281**, 211–12, Martini, *ibid.*, 1899, **29**, II, 62.

³ Meldrum and Shah, *J C S.*, 1923, **123**, 1986, Hirwe and Patil, *Proc. Ind. Acad. Sci.*, 1937, **5** (4), 321–25.

tion of chlorosalicylamide, which yields 3-chloro-salicylic acid in good quantity on hydrolysis

Methylation of the chloroacid with dimethyl sulphate and concentrated alkali affords a good yield of the *methyl ether*, hitherto unknown

5-Chlorosalicylic acid—This acid is obtained alone and not in a mixture, as obtained by previous workers⁴ if the rate of passing chlorine and the temperature is controlled, as described in the experimental section

3 5-Dichlorosalicylic acid—The rate of passing chlorine is not very important in this case. Chlorination of salicylic acid at 0°–5° gives pure dichloro acid

The *methyl ethers* of the above two acids have been obtained by chlorination of the corresponding 2-methoxy-benzoic acids, they could not be obtained by the direct methylation of the acids

The *amides* of some of the above compounds have been prepared by the usual methods

Experimental

3-Chlorosalicylic acid has been prepared by two different methods

Method I—By using (a) molecular chlorine or (b) nascent chlorine (a) Chlorine (35 g, 1 mol) was slowly passed at 0°–5° into a glacial acetic acid solution of 5-sulphosalicylic acid (100 g). The mixture was kept at room temperature overnight during which time, much hydrogen chloride was evolved and a sticky mass separated. This was filtered on glass-wool, and dried on a porous plate. It was then dissolved in a little hot water to which syrupy phosphoric acid was added to raise the boiling point, superheated steam was passed in the liquid mass, the temperature finally reaching 170°. On cooling, 3-chlorosalicylic acid separated and was filtered off and the filtrate repeatedly heated with superheated steam as before until no further yield of 3-chlorosalicylic acid was obtained. The solid was collected, washed with water and crystallised from dilute alcohol white needles, m p 180°–182° (178°–Varnholt⁵, 180°–Anschutz, Anspach⁶) yield about 72 per cent. It gave with ferric chloride an intense violet colouration

Part of the 3-chloro acid probably decomposes to chlorophenol, as indicated by the smell, during desulphonation. (b) Powdered potassium permanganate (17 g) was added slowly with constant stirring to concentrated hydrochloric acid (200 c.c.) in which was dissolved 5-sulphosalicylic acid

⁴ Heubner and Brenken and others (*loc. cit.*)

⁵ *J. Prak. Chem.*, 1887, **36** (2), 22.

⁶ *Ann.*, 1906, **348**, 312.

(50 g) The reaction mixture was kept overnight and the resulting clear solution was concentrated and then heated in a strong round-bottomed flask with addition of syrupy phosphoric acid. Superheated steam was then passed into the liquid mass for about an hour, the temperature finally reaching 170° . The smell of chlorophenol was observed also in this process. The operation was stopped when a solid product started separating. The solid was washed with water to remove potassium and manganese salts, the chloro-acid crystallised from alcohol in white needles m.p. and mixed m.p. with product from (a) $180-182^{\circ}$.

Chloral-3-chlorosalicylamide (chlorination of chloralsalicylamide)—Chlorine (5 g) was slowly passed into a solution of chloralsalicylamide (20 g) in glacial acetic acid, keeping the temperature below 15° . When the required amount of chlorine had been absorbed, the solution was kept overnight at room temperature. No solid had separated by next day. On dilution with water a pinkish powder (18 g) was precipitated which was filtered. The crude product, m.p. $132-136^{\circ}$, on crystallisation from alcohol gave colourless needles m.p., $159-160^{\circ}$ the alcoholic solution gave a red colouration with ferric chloride.

(Found N, 4.5, Cl, 44.7, $C_9H_7O_2NCl_4$ requires N, 4.4, Cl, 44.5 per cent)

3-Chlorosalicylic acid (Hydrolysis of Chloral-3-chlorosalicylamide)—Chloral-3-chlorosalicylamide (20 g) was dissolved in sodium hydroxide (10 per cent 200 c.c.) and the solution refluxed on a sand-bath for about six hours. After cooling, the solution was acidified with dilute hydrochloric acid, when a paste resulted. It was washed with water several times until it solidified. The solid crystallised from dilute alcoholic white needles with m.p. $180-81^{\circ}$. The mixed melting point of this substance with that obtained by *Method I* above showed no lowering. Yield about 86 per cent.

Potassium-3-chlorosalicylate crystallised from water in needles (Found K, 18.9, $C_7H_4O_2ClK$ requires K, 18.5 per cent)

Calcium-3-chlorosalicylate—crystallised from water in white plates (Found Ca, 9.0, H_2O , 12.2, $C_{14}H_8O_6Cl_2Ca$, $3H_2O$ requires Ca, 9.2, H_2O , 12.4 per cent)

Silver-3-chlorosalicylate—crystallised from water in minute needles turning dark on exposure (Found Ag, 38.4, $C_7H_4O_2ClAg$ requires Ag, 38.6 per cent)

3-Chlorosalicylamide Method I—A mixture of methyl-3-chlorosalicylate (20 g.) and liquor ammonia (200 c.c., D 0.888) was put in a spring-stoppered bottle and mechanically shaken for six hours when a clear

solution was obtained which on evaporation on a water-bath gave a solid. It was triturated with dilute hydrochloric acid, filtered, washed and dried (It is soluble in hot water, alcohol, acetone and acetic acid). The amide crystallised from dilute alcohol in white needles, m p $174-175^{\circ}$, it gave a violet-red colouration with ferric chloride (Found. Cl, 20.8, $C_7H_5O_2NCl$ requires Cl, 20.7 per cent.)

Method II—A mixture of 3-chlorosalicylic acid (10 g) and phosphorous pentachloride (12 g) suspended in low-boiling petroleum ether was refluxed at $30-40^{\circ}$ for four hours (Anschutz and Anspach⁷), the cool reaction mixture was poured into liquor ammonia (D 0.888), kept cool by surrounding ice, with constant stirring. The solid (8.5 g) crystallised from dilute alcohol prisms, m p $174-176^{\circ}$. Mixed melting point with the amide prepared by *Method I* above showed no lowering.

5-Chlorosalicylic acid—Salicylic acid (14 g) was dissolved in glacial acetic acid and the container surrounded with ice. Into the ice-cold solution chlorine (7 g) was gradually passed, so that the bubbles could be counted (about 60–70 bubbles per minute). The resulting solution was allowed to stand overnight at the room temperature, during which hydrogen chloride was evolved. On diluting the solution with water, a solid was obtained which crystallised from dilute alcohol in fine needles, m p $172-173^{\circ}$, yield 15 g, it gave with alcoholic ferric chloride a violet colouration (m p, 167.5° —Beulstein⁸, 172.5° —Huebner, Brenken⁹, 176° —Lassar-Cohn, Schultze¹⁰).

3,5-Dichlorosalicylic acid—Salicylic acid (14 g, 1 mol) was dissolved in glacial acetic acid and the container surrounded with ice. Into the ice-cold solution, chlorine (14 g, 2 mols) was slowly passed, the rate of bubbling chlorine did not require to be specially controlled as in the above experiment. The resulting solution was kept overnight at room temperature and then heated on a water-bath for about an hour to complete the reaction. Hydrogen chloride was profusely evolved. The reaction mixture gave a solid on dilution with water, this crystallised from dilute alcohol in thick needles, m p $219-220^{\circ}$, yield 16.5 g, it gave with alcoholic ferric chloride a reddish-violet colouration (m p 219.5° —Martin¹¹, 223° —Lassar-Cohn, Schultze¹²).

⁷ *Ibid.*

⁸ *Ber.*, 1875, 3, 810, *Ann.*, 1875, 179, 285.

⁹ *Ibid.*, 1873, 6, 174.

¹⁰ *Ibid.*, 1905, 32, 3300.

¹¹ *Gas.*, 1890, 20, II, 62.

¹² *Ber.*, 1905, 32, 3300.

Calcium-3 5-dichlorosalicylate—crystallised from water in white plates Found Ca, 7.4, H₂O, 14.0, C₁₄H₆O₆Cl₂Ca, 4H₂O requires Ca, 7.6, H₂O, 13.7 per cent)

3-Chloro-2-methoxybenzoic acid—3-Chlorosalicylic acid (17 g) was dissolved in cold potassium hydroxide (75 c.c.—40 g KOH in 150 c.c. H₂O) and dimethyl sulphate (100 g) gradually added with constant shaking and cooling under tap. It was then kept overnight and then heated on a water-bath for half an hour, when further quantity of potassium hydroxide (75 c.c. remaining from above) was added and the heating continued for quarter of an hour more. The cooled solution on acidification gave a solid (16 g) which crystallised from alcohol white needles, m.p. 120–21° it gave no colouration with alcoholic ferric chloride (Found equivalent weight, 187.4, Cl, 19.1, C₈H₇O₃Cl requires equivalent weight, 186.5, Cl, 19.0 per cent) It is soluble in alcohol, acetone, benzene and acetic acid

Sodium-3-chloro-2-methoxybenzoate—crystallised from water needles (Found Na, 10.4, H₂O, 8.1, C₈H₆O₃ClNa, H₂O requires Na, 10.2, H₂O, 8.0 per cent)

Barium-3-chloro-2-methoxybenzoate—crystallised from water white needles (Found Ba, 23.8, 23.8, C₁₆H₁₂O₆Cl₂Ba, 4H₂O requires Ba, 23.6 per cent)

Silver-3-chloro-2-methoxybenzoate—Difficultly soluble in hot water darkens (Found Ag, 37.1, C₈H₆O₃ClAg requires Ag, 36.8 per cent)

3-Chloro-2-methoxybenzamide—A mixture of 3-chloro-2-methoxybenzoic acid (6 g) and phosphorous pentachloride (7 g) was treated as above, until a yellowish-white solid (5 g) was obtained. It crystallised from alcohol flakes, m.p. 99–100° it gave no colouration with alcoholic ferric chloride (Found Cl, 19.3, C₈H₆O₃NCl requires Cl, 19.1 per cent) It is soluble in alcohol, acetone, benzene and acetic acid

5-Chloro-2-methoxybenzoic acid—2-Methoxybenzoic acid (14 g) was dissolved in glacial acetic acid and the solution kept cool by surrounding ice whilst chlorine (7 g) was passed into it. The resulting solution was allowed to stand overnight at room temperature. On dilution a solid was obtained (15.5 g) which crystallised from dilute alcohol white needles, m.p. 80–81°, it gave no colouration with alcoholic ferric chloride (m.p. 81–82°—Peratoner, Condorelli¹³)

Silver-5-chloro-2-methoxybenzoate—crystallised from water minute needles turning brownish (Found Ag, 36.9, C₈H₆O₃ClAg requires Ag, 36.8 per cent)

¹³ *Gaz.*, 1898, 28, I, 211

5-Chloro-2-methoxybenzamide—A mixture of 5-chloro-2-methoxybenzoic acid (6 g) and phosphorous pentachloride (7 g) was treated as above. A solid (5 g) was obtained. It crystallised from alcohol prisms, m p $137-138^{\circ}$, it gave no colouration with alcoholic ferric chloride (Found Cl, 19.2, $C_8H_5O_2NCl$ requires Cl, 19.1 per cent). It is soluble in alcohol, acetone, benzene and acetic acid.

3 5-Dichloro-2-methoxybenzoic acid—2-Methoxybenzoic acid (15 g) was dissolved in glacial acetic acid and the solution kept cool by surrounding ice, whilst chlorine (15 g) was passed into it. The resulting solution was kept overnight at room temperature. Next day a solid (11 g) had separated which was filtered off, washed with acetic acid and then with water and dried. It crystallised from alcohol white prisms, m p $166-167^{\circ}$. A further quantity (4 g) of the substance was recovered by diluting the mother-liquor with water. It gave no colouration with alcoholic ferric chloride (m p $166.5-167^{\circ}$ Martin¹⁴).

Sodium-3 5-dichloro-2-methoxybenzoate—crystallised from water white plates (Found Na, 8.0, H_2O , 13.2, $C_8H_5O_2Cl_2Na \cdot 2H_2O$ requires Na, 8.2, H_2O , 12.90 per cent).

Barium-3 5-dichloro-2-methoxybenzoate—crystallised from water needles (Found Ba, 20.3, H_2O , 13.2, $C_{18}H_{10}O_6Cl_4Ba \cdot 5H_2O$ requires Ba, 20.5, H_2O , 13.5 per cent).

Silver-3 5-dichloro-2-methoxybenzoate—Very difficultly soluble in water turns grey (Found Ag, 33.1, $C_8H_5O_2Cl_2Ag$ requires Ag, 32.9 per cent).

3 5-Dichloro-2-methoxybenzamide—A mixture of 3 5-dichloro-2-methoxybenzoic acid (20 g) and phosphorous pentachloride (25 g) was treated as above, when a solid (19.5 g) was obtained. It crystallised from alcohol white prisms, m p $152-153^{\circ}$, it gave no colouration with alcoholic ferric chloride (Found N, 6.0, $C_8H_4O_2NCl_2$ requires N, 6.4 per cent). It is soluble in alcohol, acetone, benzene and acetic acid.

The authors are thankful to Dr R. C. Shah for his help.

¹⁴ *Ibid.*, 1899, 29, II, 62.

NUCLEAR METHYLATION OF RESACETOPHENONE.

Preparation of 3-Methylresacetophenone and Its Derivatives.

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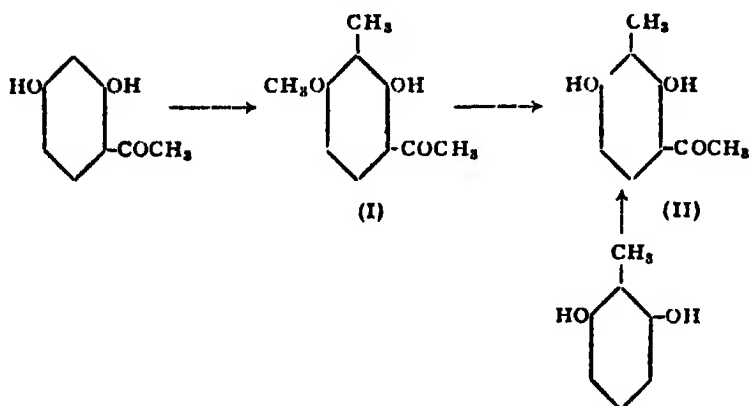
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THE reactions of resacetophenone are controlled by the existence of chelation as a consequence of which the aromatic double bonds have a tendency to get fixed Baker and Lothian¹ have shown that 2-hydroxy-4-allyloxyacetophenone on heating gives 3-allylresacetophenone thereby indicating that the 3-position is the reactive one. A similar result has been obtained by Shah and others in the condensation of resacetophenone with ethyl acetate in the presence of aluminum chloride in ether solution, the formation of the coumarin ring involving the 3-position.² Under the same conditions hydrogen cyanide introduces an aldehyde group in the 3-position in resacetophenone and its analogues.³

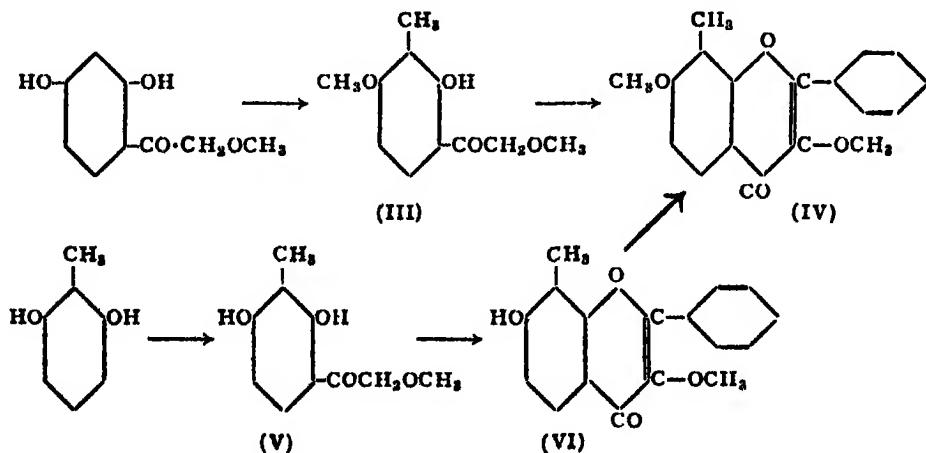
Since 3-methylresacetophenone and its derivatives were required as reference compounds and starting materials in connection with other work in progress in these laboratories and their preparation *via* 2-methyl-resorcinol is rather round about the nuclear methylation of resacetophenone and ω -methoxy-resacetophenone has now been studied.

Resacetophenone formed 2-hydroxy-3-methyl-4-methoxy-acetophenone (I) on treatment with methyl iodide and methyl alcoholic potash. This underwent demethylation to give 3-methyl-resacetophenone (II). The constitution of this compound was established by its synthesis from 2-methylresorcinol (Perkin⁴, Rangaswami and Seshadri⁵) by condensation with acetonitrile. With regard to the progress of this methylation resacetophenone resembles the esters of β -resorcylic acid, the same factors obviously being involved in both cases.

The work has been repeated with ω -methoxyresacetophenone⁶ and in this connection the assumption that the hydroxy group which undergoes etherification is the one present in the 4th position and not the one in the 2nd position has been substantiated. The product of nuclear methylation (III) easily undergoes condensation with sodium benzoate and benzoic anhydride according to the procedure developed by Allan and Robinson.⁷



and yields a flavone which has been found to be 3,7-dimethoxy-8-methyl-flavone (IV). The production of a flavone is itself sufficient proof that the 2-hydroxy group has not been affected by the process of methylation. The identity of (IV) has however been established by its synthesis starting from 2-methylresorcinol. By condensation with methoxyacetoneitrile ω -methoxy-3-methyl-resacetophenone (V) was obtained which with sodium benzoate and benzoic anhydride gave rise to 3-methoxy-7-hydroxy-8-methyl-flavone (VI) which subsequently underwent methylation easily to give (IV).



Experimental

Nuclear methylation of resacetophenone — 2-hydroxy-3-methyl-4-methoxy-acetophenone — A solution of resacetophenone (2 g) in methyl alcoholic potash containing 15 c.c of anhydrous methyl alcohol and 2.6 g of caustic potash was cooled in freezing-mixture and treated with ice-cold methyl

iodide (4.2 cc) all at once. The mixture was well shaken to render it homogeneous and the container left well stoppered in the ice-bath to assume laboratory temperature slowly. After standing overnight the mixture which had deposited a little solid was gently boiled under reflux in a water-bath for 7 hours and then poured into excess of ice-water (150 cc). The slightly pasty mass that separated overnight was filtered, washed with water and then macerated with cold dilute alkali when nearly half of it went into solution leaving the remainder as a clean solid. This insoluble portion when filtered and washed with water melted indefinitely in the neighbourhood of 80° and on crystallisation from alcohol gave 2-hydroxy-3-methyl-4-methoxy-acetophenone in the form of stout needles and micaceous plates melting at $82-3^{\circ}$ (Found C, 66.5, H, 7.0, OCH_3 , 17.3, $\text{C}_{10}\text{H}_{10}\text{O}_2$ requires C, 66.7, H, 6.7, OCH_3 , 17.2 per cent). Yield 0.6 g. The compound was easily soluble in the common organic solvents and gave a greenish blue colour with alcoholic ferric chloride.

Demethylation of above to produce 3-methylresacetophenone—The above compound (0.5 g) was dissolved in a mixture of phenol (0.5 g) and acetic anhydride (0.5 cc) and gently boiled for half an hour with hydriodic acid (sp gr 1.70, 8 cc). The resulting liquid was diluted with water (20 cc) and repeatedly ether-extracted. The combined ether-extract was shaken with sodium bicarbonate solution to remove the acetic acid and then washed with a little water. On evaporation of the solvent a dark-coloured oil was left behind. This was stirred thrice with small quantities of water which was then thrown away, so as to remove most of the phenol used. The residual oil was then dissolved in alcohol and allowed to crystallise whereby a compound melting from 141 to 146° was obtained. This on two further crystallisations from benzene gave 3-methylresacetophenone in the form of plates and needles melting at $154-5^{\circ}$ and was found to be identical with the specimen prepared from 2-methylresorcinol (see below).

3-Methylresacetophenone from 2-methylresorcinol—A solution of 2-methylresorcinol (1 g) in absolute ether (25 cc) was treated with pure acetonitrile (0.8 g) and anhydrous zinc chloride (0.5 g) and saturated with dry hydrogen chloride. The current of the gas was stopped at the end of two hours and the mixture left overnight. The clear solution that was obtained on the addition of water (25 cc) was shaken with ether to remove unchanged reactants. The pale yellow aqueous solution containing the ketimine-hydrochloride was heated for one hour in a boiling water-bath and then cooled when the ketone separated in the form of a crystalline powder. On recrystallising from methyl alcohol it was obtained as colourless needles and rectangular plates melting at $156-7^{\circ}$ (Found C, 64.6, H, 6.1, $\text{C}_9\text{H}_{10}\text{O}_2$).

requires C, 65.1, H 6.0 per cent) It gave a violet colour with alcoholic ferric chloride. A mixed melting point with the sample obtained starting from resacetophenone showed no depression.

2-Hydroxy-3-methyl- ω -4-dimethoxyacetophenone—The nuclear methylation of ω -methoxyresacetophenone was carried out according to the same procedure as was adopted in the case of resacetophenone. The reaction was more easy and the product was obtained pure more readily. The solution of the ω -methoxy ketone in alcoholic potash which set to a thick cake at the temperature of the freezing-bath was diluted with enough anhydrous methyl alcohol to enable uniform mixing and shaking, before methyl iodide was added. As the methylation proceeded big crystals of potassium iodide separated from the solution. When after refluxing for 7 hours the mixture was poured into water and left overnight the precipitated solid was found to be only slightly sticky and to melt rather sharply at 96–8°. After crystallisation from alcohol in which it was easily soluble the 3-methyl-4-methoxy ketone came down as long woolly fibres melting at 109°. (Found C, 62.4, H, 6.5, $-\text{OCH}_3$, 29.2, $\text{C}_{11}\text{H}_{14}\text{O}_4$ requires C, 62.9, H, 6.7, $-\text{OCH}_3$, 29.5 per cent.)

The substance appeared as long rectangular rods under the microscope, gave a pinkish brown colour with alcoholic ferric chloride and was insoluble in cold dilute alkali. During combustion it melted smoothly to a brown liquid, after which it decomposed to give a dark oily product which proved very refractory. Yield of the twice-crystallised product was 0.6 g from 2 g of ω -methoxyresacetophenone.

3-7-Dimethoxy-8-methylflavone from the above ketone—An intimate mixture of the ketone (1 g), sodium benzoate (1.5 g) and benzoic anhydride (4 g) was heated in an oil-bath at 200° for 4 hours under a pressure of about 40 mm of mercury. The residue was treated with a large excess of water containing a little sodium carbonate and left for some hours in order to remove the excess of benzoic anhydride. The aqueous portion was decanted off and the solid left behind treated again in the same fashion with excess of water and carbonate. A dark coloured oil remained which when dissolved in alcohol and left for some days deposited needles with a glistening yellow colour and melting at 143–45°. When recrystallised from alcohol the flavone melted at 145–46° and had the appearance of stout rectangular prisms under the microscope. (Found C, 72.9, H, 5.3, $\text{C}_{18}\text{H}_{16}\text{O}_4$ requires C, 73.0, H, 5.4 per cent). A mixed melting point showed it to be identical with the specimen prepared from 2-methylresorcinol as described below.

3-Methyl- ω -methoxyresacetophenone—The preparation of this compound from 2-methylresorcinol was very similar to that of 3-methylresaceto-

phenone Methoxyacetonitrile (b.p. 119–23°) was used instead of acetonitrile and the condensation took place even without the addition of anhydrous zinc chloride, the ketimine hydrochloride separating in a crystalline form in about 4 hours from the commencement of the reaction. When the mixture was treated with water the next day and the aqueous solution after shaking with ether was heated in a boiling water-bath the required ketone separated in the form of a crystalline powder. After recrystallisation from alcohol it came out as rectangular and hexagonal prisms melting at 203–5° (Found C, 60.8, H, 6.4, $C_{16}H_{12}O_4$ requires C, 61.2, H, 6.1 per cent). The compound was fairly soluble in hot water and easily in the common organic solvents and gave a dark violet colour with alcoholic ferric chloride.

3-Methoxy-7-hydroxy-8-methylflavone from the above ketone—An intimate mixture of the ketone (0.4 g), sodium benzoate (1 g) and benzoic anhydride (4 g) was heated under reduced pressure for 4 hours in an oil-bath at 190°. The product was then refluxed for half an hour with 10 per cent alcoholic potash (30 c.c.) to hydrolyse the 7-benzoyloxy compound first formed. Most of the alcohol was then distilled off, the residue diluted with water and the clear solution saturated with carbon dioxide. The required 7-hydroxy flavone was thus precipitated and when crystallised from alcohol was obtained in the form of rectangular plates melting at 252–3° (Found C, 71.9, H, 5.4, $C_{17}H_{14}O_4$ requires C, 72.3, H, 5.0 per cent). It did not give any colour with alcoholic ferric chloride.

3, 7-Dimethoxy-8-methylflavone from the above—The 7-hydroxy-flavone (0.2 g) was dissolved in dry acetone (15–20 c.c.) and heated under reflux on a water-bath for 16 hours with a large excess of methyl iodide (2 c.c.) and anhydrous potassium carbonate (0.4 g). The residue after evaporation of the solvent was treated with acidulated water and the water-insoluble portion filtered. The precipitate was dissolved in a slight excess of alcohol and the solution filtered from insoluble matter and allowed to stand. Beautiful crystals separated in the course of a few days which after filtering and washing with a few drops of cold alcohol melted at 135–6°. After another crystallisation from aqueous alcohol the methyl ether was obtained as pale yellow needles which melted at 141–2° and appeared as rectangular rods under the microscope (Found C, 72.8, H, 5.6, $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.4 per cent). It was identical in all respects with the one prepared from 2-hydroxy-3-methyl- ω 4-dimethoxyacetophenone.

Summary

The methylation of resacetophenone and its ω -methoxy derivative using methyl iodide and methyl alcoholic potash has been studied. The former

gave 2-hydroxy-3-methyl-4-methoxyacetophenone the constitution of which was established by demethylation to 3-methylresacetophenone and comparison with a specimen prepared from 2-methylresorcinol. In the same way ω -methoxyresacetophenone gave 2-hydroxy-3-methyl- ω -4-dimethoxyacetophenone which was subsequently converted to 3,7-dimethoxy-8-methylflavone. The identity of this flavone was proved by its synthesis from 2-methyl-resorcinol.

It is concluded that under the above conditions resacetophenone undergoes nuclear methylation in the 3-position and that the hydroxyl group in the 4th position gets etherified.

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A FINE ADJUSTMENT DEVICE FOR USE WITH THE MICRO-DUMAS APPARATUS.

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(Communicated by Prof T R. Seshadri)

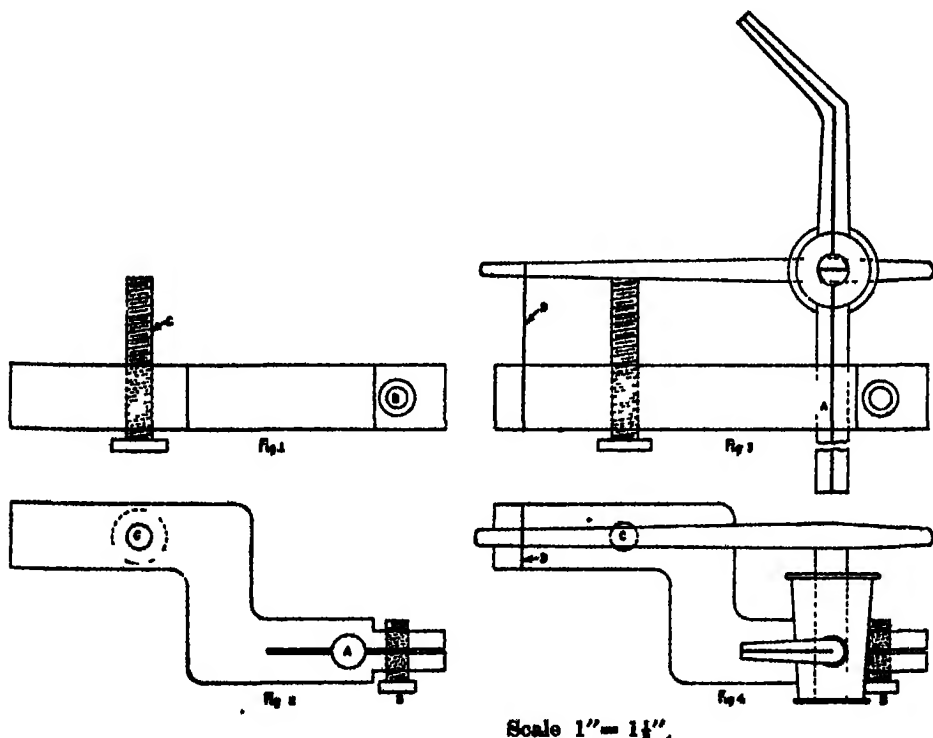
It is well known that in the determination of nitrogen in organic compounds by the method of Pregl (*Quantitative Organic Micro-Analysis* by Pregl—2nd and 3rd English editions) the accuracy of the experiment depends on the rate of combustion of the compound, which is controlled by observing the rate of entry of gas bubbles into the nitrometer past the mercury seal. To obtain a good value not only should the preliminary combustion of the compound be carried out at the optimum rate which gives rise to not more than two bubbles in every three seconds, but the subsequent washing out of the products of combustion from the combustion tube into the nitrometer by means of carbon dioxide from the Kipp should be done so carefully that a gas rate of two bubbles in three seconds is not exceeded even for a few seconds. The latter operation requires considerable experience as a higher gas rate invariably gives higher values for nitrogen than according to the theory.

For the delicate manipulation of the stop-cock in the connecting piece various devices have been tried in the past, the most satisfactory being the provision of the stop-cock with a long handle so that by the application of gentle pressure to the tip of the handle small rotations of the barrel can be effected. The cutting of shallow channels about 4 mm long on the surface of the barrel at either end of the main bore has considerably added to the value of the long handle, and ensures accurate results to the careful and diligent worker (*loc cit*).

The above combination suffers from one or two drawbacks. The barrel of the stop-cock must be greased to a certain optimum extent. While over-greasing fills up part of the channel and makes the stop-cock turn round of its own accord owing to the weight of the long handle, under-greasing brings in its train a considerable amount of friction and a corresponding diminution in the benefit derived from the long handle. Further the beginner generally does not know the right amount of pressure to be applied to the tip of the handle for effecting a certain desired rotation of the barrel with

the result that the gas velocity is not completely under his control. The use of the simple device described in this paper while being considerably helpful even to the expert micro-analyst, makes the determination safe even in the hands of the beginner.

Figs. 1 and 2 give the plan and the elevation of the device which consists of an ebonite piece carrying two screws, while Figs 3 and 4 represent the same when it is fixed on to the connecting piece. The non-tapering portion of the connecting piece can easily pass through the hole (A) and the ebonite piece fixed rigidly at any desired position on the glass part by means of the screw (B) which controls the cleft shown. The screw (C) controls the movement of the stop-cock, every forward movement tending to close the



channel in the stop-cock while every backward movement has the opposite effect. The ebonite piece is fixed at such a position that the stop-cock is completely closed when the screw can advance no farther. By gradually working it backwards the stop-cock is gently opened by the action of the elastic band (D) and it is possible by turning the milled head of the screw by about 5 or 10° at a time to get any gas speed required. Whenever during the

course of the experiment it is necessary to have the long handle parallel to the body of the connecting piece so as to get a straight passage for the gas, the band can be slipped off and the handle taken to any desired position

The device has been tested in a number of estimations and found very satisfactory. It is easily fixed to the connecting piece and any desired gas speed obtained and maintained without any difficulty. There is no strain on any part of the apparatus because of the shape of the ebonite piece the weight of which is small. The part is easy to construct and costs little. It was made in the Instruments Section of this University.

The author's thanks are due to Dr G. Gangadharam for the drawings.

GENERALIZATION OF A THEOREM OF DICKSON.

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Received September 26, 1938
(Communicated by Dr S Chowla)

1 DICKSON¹ showed that the congruence

$$x^k + y^k + 1 \equiv 0 \pmod{p}$$

always has a solution with $xy \not\equiv 0 \pmod{p}$

$$\text{if } p > (k-1)^2(k-2)^2 + 6k - 2,$$

where k and p are odd primes

In this paper I give a simple proof, by a different method based on lemmas due to Hardy and Littlewood, of this result in the generalized form.

THEOREM Let p denote a prime and let n be prime to p , then the number N , of solutions of

$$x^k + y^k \equiv n \pmod{p}$$

$$1 < x < p, \quad 1 < y < p, \quad xy \not\equiv 0 \pmod{p}$$

satisfies

$$N > p - (k-1)(k-2)\sqrt{p} - (3k-1)$$

and hence there is always a solution, if

$$p \geq (k-1)^2(k-2)^2 + 6k - 2$$

provided $k \geq 6$.

It is curious that the lower limit for p obtained by our method is exactly the same as that obtained by Dickson. Incidentally we give a new proof of a recent result due to Davenport and Hasse.²

2 *Notation* In this section k is any fixed integer ≥ 6 .

$S_p = \sum_{k=1}^q \rho^{ak}$ where ρ is a primitive q th root of unity, i.e., $\rho = e^{2\pi i a/q}$ where $(a, q) = 1$.

¹ *Jour für Math.*, 135, (1909), 181-88

See also A. Hurwitz (*Journal für Mathematik*, 136, (1909), pp. 272-92, who also generalizes the theorem in question by other methods.

² *Crelle's Journal*, 172, (1934), 151-82. The equation (1) below is also proved in their paper.

$A(q) = A(q, n) = q^{-1} \sum_{\rho} (S_{\rho})^2 \rho^{-n}$ where ρ runs over the $\phi(q)$ primitive q th roots of unity

$M(p, n)$ is the number of solutions of $h_1^k + h_2^k = n \pmod{p}$ where $0 \leq h_1 < p, 0 \leq h_2 < p$

*Lemma 1*³

$$1 + A(p) = p^{-1} M(p, n).$$

Lemma 2 If $p \nmid n$,

$$|A(p)| \leq \frac{(k-1)(k-2)}{\sqrt{p}} + \frac{k-1}{p}$$

Proof. Write $\epsilon = e^{2\pi i/p}$, and for each character $\chi \pmod{p}$

$$\tau_{\chi} = \sum_{l=1}^{p-1} \epsilon^l \chi(l) = \sum_l \epsilon^l \chi(l)$$

We have (LV, satz 308)

$$\tau_{\chi_0} = -1 \text{ (where } \chi_0 \text{ is the principal character) } |\tau_{\chi}| = \sqrt{p} \text{ (} \chi \neq \chi_0 \text{)}$$

The $\delta = (k, p-1)$ characters χ with the property that $\chi^k = \chi_0$ (LV, satz 309) are called "special characters" and will be denoted by the letter $\psi, \psi_0 = \chi_0$

We have (LV, satz 310) when

$$q = p, \quad \rho = \epsilon^r, \quad \text{where } (r, p) = 1,$$

$$S_{\rho} = \sum_{\psi \neq \psi_0} \psi(r) \tau_{\bar{\psi}}$$

We have also (LV, satz 317)

$$\begin{aligned} A(p) &= p^{-1} \sum_{\psi_1, \psi_2} \tau_{\psi_1} \tau_{\bar{\psi}_2} \sum_{r=1}^{p-1} \epsilon^{\frac{2\pi i r n}{p}} \bar{\psi}_1(r) \bar{\psi}_2(r) \\ &= p^{-1} \left\{ \sum'_{\psi_1, \psi_2} () + \sum''_{\psi_1, \psi_2} () \right\} \end{aligned}$$

[where ψ_1, ψ_2 run independently over the $(\delta-1)$ special characters $\psi \neq \psi_0$ and in Σ' the summation is for ψ_1, ψ_2 subject to $\bar{\psi}_1 \bar{\psi}_2 \neq \chi_0$ and in Σ'' the ψ_1, ψ_2 satisfy $\bar{\psi}_1 \bar{\psi}_2 = \chi_0$. The number of terms in Σ' is $(\delta-1)^2$. The number of terms in Σ'' is $\delta-1$ and hence in Σ' there are $(\delta-1)$, $(\delta-2)$ terms. Now we have

$$|\tau_{\psi_1} \tau_{\bar{\psi}_2}| = p.$$

³ E. Landau, *Vorlesungen über Zahlentheorie*, 1, satz 286. We refer to this book as LV.

The inner sum is, since every time $\bar{\psi}_1(r) \bar{\psi}_2(r)$ is a character $\chi(r)$ [and without loss of generality $0 < n < p$]

$$\begin{aligned} &= \sum_{r=1}^{p-1} e^{-rn} \chi(r) = \sum_{r=1}^{p-1} e^{r(p-n)} \chi(r) \\ &= \bar{\chi}(p-n) \sum_{r=1}^{p-1} e^{r(p-n)} \chi[r(p-n)] \\ &= \bar{\chi}(p-n) \sum_{r=1}^{p-1} e^r \chi(r) = \bar{\chi}(p-n) \tau_{\chi} \end{aligned}$$

Hence

$$|E| \leq |E'| + |E''| \leq (\delta-1)(\delta-2)(p\sqrt{p} + (\delta-1)p). 1.$$

whence

$$|A(p)| < \frac{(\delta-1)(\delta-2)}{\sqrt{p}} + \frac{\delta-1}{p} < \frac{(k-1)(k-2)}{\sqrt{p}} + \frac{k-1}{p}.$$

3. *Concluding argument* We observe that from lemmas 1 and 2

$$|p^{-1} M(p, n) - 1| \leq \frac{(k-1)(k-2)}{\sqrt{p}} + \frac{k-1}{p}$$

whence

$$(1) \quad M(p, n) \geq p - (k-1)(k-2)\sqrt{p} - (k-1)$$

It is easily seen that

$$\begin{aligned} N &\geq M(p, n) - 2k \geq p - (k-1)(k-2)\sqrt{p} - (k-1) - 2k \\ &= p - (k-1)(k-2)\sqrt{p} - (3k-1) \end{aligned}$$

and therefore $N > 0$ if

$$\sqrt{p} > \alpha = \frac{(k-1)(k-2) + \sqrt{(k-1)^2(k-2)^2 + 4(3k-1)}}{2}$$

where α is the larger root of

$$x^2 - (k-1)(k-2)x - (3k-1) = 0.$$

Now,

$$\begin{aligned} \alpha &= (k-1)(k-2) \left\{ \frac{1}{2} + \frac{1}{2} \sqrt{1 + \frac{4(3k-1)}{(k-1)^2(k-2)^2}} \right\} \\ &< (k-1)(k-2) \left\{ \frac{1}{2} + \frac{1}{2} \left(1 + \frac{1}{2} \cdot \frac{4(3k-1)}{(k-1)^2(k-2)^2} \right) \right\} \end{aligned}$$

since $\sqrt{1+z} < 1 + \frac{1}{2}z$ for $z > 0$. Thus

$$\alpha < (k-1)(k-2) + \frac{3k-1}{(k-1)(k-2)}$$

$$\alpha^2 < (k-1)^2(k-2)^2 + 2(3k-1) + \left\{ \frac{3k-1}{(k-1)(k-2)} \right\}^2$$

Hence $N > 0$ if

$$p > (k-1)^2 (k-2)^2 + 6k - 2 + \left\{ \frac{3k-1}{(k-1)(k-2)} \right\}^2$$

i.e., if

$$(2) \quad p > (k-1)^2 (k-2)^2 + 6k - 2$$

since

$$\frac{3k-1}{(k-1)(k-2)} < 1 \quad \text{for } k \geq 7$$

But since the right-hand side of (2) is a multiple of 2, (2) is equivalent to (3) $p > (k-1)^2 (k-2)^2 + 6k - 2$. Thus $N > 0$ if p satisfies (3) and our theorem is proved.

NOTE ON HARMONIC FUNCTIONS.

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§1 Introduction

ACCORDING to a well-known theorem of Gauss, every function u regular and harmonic in a region G possesses, for every sphere S —centre $P(x, y, z)$ and radius R —lying entirely inside G , the mean value property

$$\lim_{R \rightarrow 0} \frac{1}{4\pi R^2} \int \int_S u(Q) dS_Q = u(P) \quad (1)$$

The converse of this theorem, that if u is continuous and possesses the property (1) for every sphere in G then u is harmonic in G , was discovered by Bôcher and Koebe. In other words, the property (1) is a characteristic one for functions harmonic in G . A number of conditions each of which characterises a harmonic function have since been given. For instance Zaremba¹ proved that if

$$\lim_{h \rightarrow 0} \frac{1}{h^2} \left[\sum_{i,j,k} \{u(x+h, y, z) + u(x-h, y, z)\} - 6u(x, y, z) \right] = 0$$

then $\nabla^2 u = 0$. The condition (1) was generalised by Blaschke² and may be stated as follows. A necessary and sufficient condition that the continuous function u be harmonic in G is

$$\lim_{R \rightarrow 0} \frac{1}{R^2} \left[\frac{1}{4\pi R^2} \int \int_S u(Q) dS_Q - u(P) \right] = 0 \quad (2)$$

for every sphere S in G . Results similar to those of Zaremba and Blaschke have been recently obtained by Kappos³. Saks⁴ has used Blaschke's theorem to derive two other properties either of which may be regarded as the defining property of harmonic functions. In this paper it will be shown that results analogous to those of Blaschke and Saks may be obtained for solutions of Poisson's equation and also of the equation $\nabla^2 u + cu = 0$. The following results are obtained.

$$(I) \text{ If } \lim_{R \rightarrow 0} \frac{1}{R^2} \left[\frac{1}{4\pi R^2} \int \int_S u dS - u(P) + \int \int \int \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau \right] = 0,$$

$$\text{then } \nabla^2 u + 4\pi\mu = 0$$

$$(II) \text{ If } \lim_{R \rightarrow 0} \frac{1}{R^3} \left[\frac{1}{4\pi R^3} \int_S u \, dS - u(P) \frac{f(R)}{f(0)} \right] = 0,$$

$$\text{then } \nabla^2 u - \frac{3f''(0)}{f(0)} u = 0.$$

The first reduces to Blaschke's theorem for $\mu = 0$ and the second is the converse of a mean-value theorem due to Weber⁵. Making the same use of theorems I and II as Saks has done of Blaschke's theorem, the following further results are obtained.

$$(III) \text{ If } \lim_{R \rightarrow 0} \frac{1}{2R} \left[\frac{1}{4\pi} \int_S \frac{\partial u}{\partial R} \, d\Omega + \frac{1}{R^2} \int_K \int \mu \, d\tau \right] = 0,$$

$$\text{then } \nabla^2 u + 4\pi\mu = 0$$

(IV) Let $\nabla^2 v = 0$ and $v \neq 0$. Then, if

$$\lim_{R \rightarrow 0} \frac{1}{R^3} \left[\frac{1}{4\pi} \int_S \left(v \frac{\partial u}{\partial R} - u \frac{\partial v}{\partial R} \right) \, dS + \int_K \int v\mu \, d\tau \right] = 0,$$

$$\nabla^2 u + 4\pi\mu = 0.$$

$$(V) \text{ If } \lim_{R \rightarrow 0} \frac{1}{4\pi R} \int_S \frac{\partial u}{\partial R} \, d\Omega = cu(P), \text{ then } \nabla^2 u - 3c u = 0$$

The theorems III and IV correspond to those of Saks, to which they reduce when $\mu = 0$. The restrictions imposed on the functions u , μ , f in these theorems are mentioned below, in the proper contexts.

§2 A Lemma

Let $P(x, y, z)$ be an interior point of G and let the function $\psi(x, y, z, r) = \psi(P, r)$ satisfy the conditions. (i) $\psi(x, y, z, r)$ is continuous in all its arguments, and (ii) $\lim_{r \rightarrow 0} \psi(x, y, z, r) = 0$. Then if

$$J(P) = \frac{1}{a^3} \int_0^a r^4 \psi(P; r) \, dr$$

we have

$$\lim_{P' \rightarrow P} \frac{J(P') - J(P)}{P'P} = 0 \quad (2.1)$$

In fact we may choose axes so that PP' is parallel to the z -axis. Let $(x, y, z + h)$ be the co-ordinates of P' . Then

$$\frac{J(P') - J(P)}{P'P} = \frac{1}{a^3} \int_0^a \frac{\psi(P'; r) - \psi(P; r)}{h} r^4 \, dr$$

Since $\psi(P, r) \rightarrow 0$ as $r \rightarrow 0$ we can find r_0 such that $|\psi(P, r)| < \frac{h^2}{2}$ for $r < r_0$, and since $\psi(P, r) = \psi(x, y, z, r)$ is continuous in all its arguments

this continuity will be uniform. Then r_0 will depend upon h only, $r_0 = r_0(h)$, and the above inequality will hold also for $\psi(P', r)$ with the same r_0 . Since the upper limit a in $J(P)$ is arbitrary we may choose it so that $a < r_0(h)$. We then have

$$\left| \frac{J(P') - J(P)}{P'P} \right| = \left| \frac{1}{a^3} \int_0^a \frac{\psi(P'; r) - \psi(P, r)}{h} r^4 dr \right|$$

$$< \frac{h}{a^3} \int_0^a r^4 dr = \frac{1}{5} ha^2$$

from which it is evident that $\lim_{P' \rightarrow P} \frac{J(P') - J(P)}{P'P} = 0$.

This proves the lemma. I am not aware of the proof given by Blaschke of his theorem, but it must be noticed that his theorem is an immediate consequence of our lemma. For writing

$$\psi(P; R) = \frac{1}{R^3} \left[\frac{1}{4\pi R^3} \int_S u(Q) dS_Q - u(P) \right]$$

so that if u is continuous, ψ satisfies the conditions of the lemma.

We then have $u(P) = \frac{1}{4\pi R^3} \int_S u(Q) dS_Q - R^3 \psi(P, R)$

and integrating from 0 to a wrt R , we get

$$u(P) = \frac{3}{4\pi a^3} \iiint_K u d\tau - \frac{3}{a^3} \int_0^a R^4 \psi(P; R) dR$$

[K is the volume inside a sphere of rad a and centre P]

$$= I(P) - J(P).$$

To calculate $\frac{\partial u_P}{\partial x}$, for instance, we take $P'(x, y, z+h)$ and compute the limit $\lim_{h \rightarrow 0} \frac{u(P') - u(P)}{h}$. The lemma shows that $J(P)$ disappears in this process and we have

$$\frac{\partial u}{\partial x} = \lim_{h \rightarrow 0} \frac{I(P') - I(P)}{h}.$$

From this point onwards the argument runs on the usual lines* and we infer the existence and continuity of the second derivatives of u . We now have by Green's theorem

$$\frac{1}{4\pi R^3} \int_S u(Q) dS_Q - u(P) = \frac{1}{4\pi} \int_K \int \left(\frac{1}{r} - \frac{1}{R} \right) \nabla^2 u d\tau,$$

where r = distance of $d\tau$ from P , the centre of the sphere.

$$\begin{aligned} \lim_{R \rightarrow 0} \frac{1}{R^2} \left[\frac{1}{4\pi R^2} \int_S u(Q) dS_Q - u(P) \right] \\ = \lim_{R \rightarrow 0} \frac{1}{4\pi R^2} \int_K \int \int \left(\frac{1}{r} - \frac{1}{R} \right) \nabla^2 u d\tau \\ = (\nabla^2 u)_P \cdot \lim_{R \rightarrow 0} \frac{1}{4\pi R^2} \int_K \int \int \left(\frac{1}{r} - \frac{1}{R} \right) d\tau \\ = \frac{1}{6} (\nabla^2 u)_P \end{aligned}$$

Since the value of the left-hand side is zero, it follows that $\nabla^2 u = 0$. This proves the sufficiency of the condition. Since by Gauss's theorem the condition is evidently necessary, we have herewith proved Blaschke's theorem.

§3 Poisson's Equation

Let μ be a given function continuously differentiable in G . Let u be continuous in G and let it satisfy further, for every sphere in G , the condition

$$\lim_{R \rightarrow 0} \frac{1}{R^2} \left[\frac{1}{4\pi R^2} \int_S u(Q) dS_Q - u(P) + \int_K \int \int \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau \right] = 0 \quad (3.1)$$

Put

$$\psi(P, R) = \frac{1}{R^2} \left[\frac{1}{4\pi R^2} \int_S u(Q) dS_Q - u(P) + \int_K \int \int \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau \right]$$

so that

$$u(P) = \frac{1}{4\pi R^2} \int_S u(Q) dS_Q + \int_K \int \int \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau - R^2 \psi(P, R)$$

Multiplying by R^2 and integrating from 0 to R w.r.t. R , this gives

$$\begin{aligned} u(P) = \frac{3}{4\pi R^2} \int_K \int \int u d\tau + \int_K \int \int \frac{(R-r)^2(2R+r)}{2rR^2} \mu d\tau \\ - \frac{3}{R^2} \int_0^R R^4 \psi(P, R) dR \end{aligned}$$

$$= I(P) + L(P) - J(P)$$

Taking P' to be the point $(x, y, z+h)$, we compute as before $\frac{\partial u_P}{\partial z} = \lim_{h \rightarrow 0} \frac{u(P') - u(P)}{h}$. In this process the integral $J(P)$ will disappear by the

Lemma. If μ is continuously differentiable, then $\mu_1 = \frac{(R-r)^2(2R+r)}{2rR^2} \mu$ is also continuous and continuously differentiable and by a well-known

theorem in Potential Theory I, $(P) = \iiint_K \frac{\mu_1}{r} d\tau$ possesses continuous second derivatives. We may now apply the usual type of reasoning to I (P) and infer the existence of continuous second derivatives for I (P). Thus we conclude that under the given condition u is twice continuously differentiable. But if this is so we have

$$\begin{aligned} \lim_{R \rightarrow 0} \frac{1}{R^3} \left[\frac{1}{4\pi R^3} \int_S u(Q) dS_Q - u(P) \right] \\ = \lim_{R \rightarrow 0} \frac{1}{R^3} \frac{1}{4\pi} \iiint_K \left(\frac{1}{r} - \frac{1}{R} \right) \nabla^2 u d\tau \\ = (\nabla^2 u)_P \lim_{R \rightarrow 0} \frac{1}{4\pi R^3} \iiint_K \left(\frac{1}{r} - \frac{1}{R} \right) d\tau \\ = \frac{1}{6} (\nabla^2 u)_P \end{aligned}$$

while

$$\begin{aligned} \lim_{R \rightarrow 0} \frac{1}{R^3} \iiint_K \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau = \mu_P \cdot \lim_{R \rightarrow 0} \frac{1}{R^3} \iiint_K \left(\frac{1}{r} - \frac{1}{R} \right) d\tau \\ = \frac{4\pi}{6} \mu_P \end{aligned}$$

Hence the given condition is equivalent to

$$\nabla^2 u + 4\pi\mu = 0$$

We have thus the result

If u is continuous in G and satisfies the condition (3.1) for every sphere in G , then $\nabla^2 u + 4\pi\mu = 0$

For $\mu = 0$, this reduces to Blaschke's theorem. The condition (3.1) will be satisfied in particular if for every sphere in G

$$u(P) = \frac{1}{4\pi R^3} \int_S u(Q) dS_Q + \iiint_K \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau \quad (3.2)$$

Thus if the continuous function u satisfies the condition (3.2) for every sphere in G , then u satisfies Poisson's equation at every point of G . This is an extension to Poisson's equation of the converse theorem of Bocher and Koebe, and is well known.

§4 Pockels' Equation

Next consider the equation $\nabla^2 u + cu = 0$. Every regular solution of this equation satisfies the mean-value property

$$\frac{1}{4\pi R^3} \int_S u(Q) dS_Q = u(P) \cdot \frac{\sin R \sqrt{c}}{R \sqrt{c}} \quad (4.1)$$

a result due to Weber We may prove a converse theorem in this case, similar to that of Blaschke Let $f(x)$ be twice continuously differentiable, with $f(0)$ finite, $\neq 0$, and $f'(0) = 0$ Let the continuous function u satisfy the condition

$$\lim_{R \rightarrow 0} \psi(P, R) = 0$$

where

$$\psi(P, R) = \frac{1}{R^3} \left[\frac{1}{4\pi R^3} \int_S \int u(Q) dS_Q - u(P) \frac{f(R)}{f(0)} \right]$$

We then have

$$\frac{f(R)}{f(0)} u(P) = \frac{1}{4\pi R^3} \int_S \int u(Q) dS_Q - R^3 \psi(P, R)$$

Multiplying by R^3 and integrating from 0 to a wrt R we get

$$C u(P) = \frac{1}{4\pi} \int_K \int \int u d\tau - \int_0^a R^4 \psi(P; R) dR$$

with

$$C = \int_0^a \frac{f(R)}{f(0)} R^3 dR$$

By reasoning exactly as before we conclude that $u(P)$ is twice continuously differentiable

Now

$$\begin{aligned} & \frac{1}{R^3} \left[\frac{1}{4\pi R^3} \int_S \int u(Q) dS_Q - u(P) \frac{f(R)}{f(0)} \right] \\ &= \frac{1}{R^3} \left[\frac{1}{4\pi R^3} \int_S \int u(Q) dS_Q - u(P) \right] - \frac{u(P)}{f(0)} \cdot \frac{f(R) - f(0)}{R^3} \end{aligned}$$

Since u is twice continuously differentiable

$$\lim_{R \rightarrow 0} \frac{1}{R^3} \left[\frac{1}{4\pi R^3} \int_S \int u(Q) dS_Q - u(P) \right] = \frac{1}{6} (\nabla^2 u)_P;$$

and

$$\lim_{R \rightarrow 0} \frac{f(R) - f(0)}{R^3} = \frac{1}{2} f''(0)$$

Thus the assumed condition leads to $\nabla^2 u - \frac{3f''(0)}{f(0)} u = 0$. We have thus obtained the following result :

If u be continuous in G and if for every sphere in G

$$\lim_{R \rightarrow 0} \frac{1}{R^3} \left[\frac{1}{4\pi R^2} \int_S u(Q) dS_Q - u(P) \frac{f(R)}{f(0)} \right] = 0 \quad (4.2)$$

then $\nabla^2 u + cu = 0$ with $c = -3 f''(0)/f(0)$, provided that $f(x)$ satisfies the conditions specified above

In particular if $f''(0) = 0$, then u must be harmonic. The condition (4.2) will be satisfied if for every sphere in G

$$\frac{1}{4\pi R^2} \int_S u(Q) dS_Q = u(P) \frac{f(R)}{f(0)}.$$

Taking $f(x) = \frac{\sin \sqrt{c} \cdot x}{\sqrt{c} \cdot x}$ we obtain the converse of Weber's mean-value theorem

§5 Generalisations to n Dimensions

These results may immediately be generalised to n dimensions. Thus taking the case of Poisson's equation, the corresponding result will here be as follows. Let u be continuous in G and let it satisfy for every sphere Ω_R , centre P and radius R , in G , the condition

$$\begin{aligned} \lim_{R \rightarrow 0} \frac{1}{R^3} \left[\frac{1}{\omega_n R^{n-1}} \int_{\Omega_R} \dots \int u(Q) d\Omega - u(P) \right. \\ \left. + \frac{1}{n-2} \int \int_{K_R} \dots \int \left(\frac{1}{r^{n-1}} - \frac{1}{R^{n-1}} \right) \mu d\tau \right] = 0 \end{aligned} \quad (5.1)$$

where K_R is the volume inside Ω_R , μ is a continuously differentiable function, and ω_n is the surface-area of the unit sphere in n dimensions. Then u is twice continuously differentiable and satisfies in G the equation

$$\nabla^2 u + \omega_n \mu = 0$$

where now

$$\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \dots + \frac{\partial^2}{\partial x_n^2}.$$

In fact the proof of the differentiability of u proceeds exactly as before and then we have, by the corresponding form of Green's theorem in n dimensions,

$$\begin{aligned} \frac{1}{R^3} \left[\frac{1}{\omega_n R^{n-1}} \int_{\Omega_R} \dots \int u d\Omega - u(P) \right] \\ = \frac{1}{\omega_n (n-2)} \cdot \frac{1}{R^3} \int \int_{K_R} \dots \int \left(\frac{1}{r^{n-1}} - \frac{1}{R^{n-1}} \right) \nabla^2 u d\tau \end{aligned}$$

so that

$$\begin{aligned} \lim_{R \rightarrow 0} \frac{1}{R^2} \left[\frac{1}{\omega_n R^{n-1}} \int_{\Omega_R} \cdot \int u d\Omega - u(P) \right] \\ = \frac{(\nabla^2 u)_P}{\omega_n (n-2)} \lim_{R \rightarrow 0} \frac{1}{R^2} \iint_{K_R} \cdots \int \left(\frac{1}{r^{n-2}} - \frac{1}{R^{n-2}} \right) d\tau \\ = \frac{(\nabla^2 u)_P}{\omega_n (n-2)} \lim_{R \rightarrow 0} \frac{1}{R^2} \int_0^R \left(\frac{1}{r^{n-2}} - \frac{1}{R^{n-2}} \right) \omega_n r^{n-1} dr \\ = \frac{1}{2n} (\nabla^2 u)_P \end{aligned}$$

$$\text{and } \lim_{R \rightarrow 0} \frac{1}{R^2} \frac{1}{n-2} \iint_{K_R} \cdot \int \left(\frac{1}{r^{n-2}} - \frac{1}{R^{n-2}} \right) \mu d\tau = \frac{\omega_n}{2n} \mu_P$$

Thus u satisfies the equation $\nabla^2 u + \omega_n \mu = 0$

Again let u be continuous in G and satisfy the condition

$$\lim_{R \rightarrow 0} \frac{1}{R^2} \left[\frac{1}{\omega_n R^{n-1}} \int_{\Omega_R} \cdot \int u d\Omega - u(P) \frac{f(R)}{f(0)} \right] = 0 \quad (5.2)$$

$f(x)$ being such that $f(0) \neq 0$, $f'(0) = 0$, $f''(x)$ continuous. Then u satisfies the equation

$$\nabla^2 u - \frac{nf''(0)}{f(0)} u = 0$$

For the differentiability of u being proved exactly as before we have

$$\lim_{R \rightarrow 0} \frac{1}{R^2} \left[\frac{1}{\omega_n R^{n-1}} \int_{\Omega_R} \cdots \int u d\Omega - u(P) \right] \frac{u(P)}{f(0)} \lim_{R \rightarrow 0} \frac{f(R) - f(0)}{R^2}$$

$$= \frac{1}{2n} (\nabla^2 u)_P = \frac{1}{2} \frac{f''(0)}{f(0)} u_P$$

or

$$\nabla^2 u - \frac{nf''(0)}{f(0)} u = 0 \quad (5.3)$$

The result will be true in particular if we replace the condition (5.2) by

$$\frac{1}{\omega_n R^{n-1}} \int_{\Omega_R} \cdots \int u d\Omega = u(P) \cdot \frac{f(R)}{f(0)} \quad (5.4)$$

This result that under the condition (5.4) u satisfies the equation (5.3) has been proved as a particular case of a more general theorem and in a different way by H. Poinitsky in a recent paper ⁸

§6 Analogues of Saks's Theorems

Consider first the case of Poisson's equation. Then the analogues of Saks's theorems to this case may be stated as follows

(1) Let u be continuous, with its first partial derivatives, in G and let it satisfy for every sphere in G the condition

$$\lim_{R \rightarrow 0} \frac{1}{2R} \left[\frac{1}{4\pi} \iint_S \frac{\partial u}{\partial R} d\Omega + \frac{1}{R^2} \iiint_K \mu d\tau \right] = 0 \quad (6.1)$$

where μ is continuously differentiable. Then $\nabla^2 u + 4\pi\mu = 0$ (Here $d\Omega$ means the element of area on the unit sphere.)

(11) Let $\nabla^2 v = 0$, $v \neq 0$, in G . If u be continuous, with its partial derivatives, in G and satisfies for every sphere in G the condition

$$\lim_{R \rightarrow 0} \frac{1}{R^3} \left[\frac{1}{4\pi} \iint_S \left(v \frac{\partial u}{\partial R} - u \frac{\partial v}{\partial R} \right) dS + \iiint_K v \mu d\tau \right] = 0 \quad (6.2)$$

then u satisfies $\nabla^2 u + 4\pi\mu = 0$

The method of proof is identical with that used by Saks, except that whereas Saks makes use of Blaschke's theorem, we here use the analogue of Blaschke's theorem proved in § 3 above, from which the first theorem is an immediate consequence. Following an ingenious procedure due to Saks we may write

$$\psi(R) = \frac{1}{R^2} \left[\frac{1}{4\pi R^2} \iint_S u dS - u(P) + \iiint_K \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau \right]$$

and apply l'Hospital's rule of the differential calculus to find $\lim_{R \rightarrow 0} \psi(R)$

This procedure gives

$$\begin{aligned} \lim_{R \rightarrow 0} \psi(R) &= \lim_{R \rightarrow 0} \frac{1}{2R} \frac{d}{dR} \left[\frac{1}{4\pi R^2} \iint_S u dS - u(P) \right. \\ &\quad \left. + \iiint_K \left(\frac{1}{r} - \frac{1}{R} \right) \mu d\tau \right] \\ &= \lim_{R \rightarrow 0} \frac{1}{2R} \left[\frac{1}{4\pi} \iint_S \frac{\partial u}{\partial R} d\Omega + \frac{1}{R^2} \iiint_K \mu d\tau \right]. \end{aligned}$$

If therefore the right-hand limit vanishes, so does $\lim_{R \rightarrow 0} \psi(R)$ and hence by the theorem of § 3, u satisfies $\nabla^2 u + 4\pi\mu = 0$. This proves theorem (1). The second theorem now follows from the first, exactly as in Saks's paper. Finally consider the analogue of Saks's theorem with respect to the equation $\nabla^2 u + cu = 0$. Let u be continuous, with its first partial derivatives, in G

and let $f(x)$ satisfy the conditions specified in § 4. If we now write

$$\psi(R) = \frac{1}{R^2} \left[\frac{1}{4\pi} \int_S u d\Omega - u(P) \frac{f(R)}{f(0)} \right]$$

we find as above

$$\lim_{R \rightarrow 0} \psi(R) = \lim_{R \rightarrow 0} \frac{1}{2R} \left[\frac{1}{4\pi} \int_S \frac{\partial u}{\partial R} d\Omega - u(P) \frac{f'(R)}{f'(0)} \right]$$

Under the hypotheses regarding $f(x)$ we have

$$\lim_{R \rightarrow 0} \frac{f'(R)}{R} = \lim_{R \rightarrow 0} \frac{f'(R)}{R} - \frac{f'(0)}{R} = f''(0)$$

We thus find that if

$$\lim_{R \rightarrow 0} \left[\frac{1}{4\pi R} \int_S \frac{\partial u}{\partial R} d\Omega - u(P) \frac{f''(0)}{f'(0)} \right] = 0$$

then $\lim_{R \rightarrow 0} \psi(R) = 0$ and hence by § 4, u satisfies $\nabla^2 u - \frac{3f''(0)}{f'(0)} u = 0$

Writing $c = \frac{f''(0)}{f'(0)}$, this result may be stated as follows

If u be continuous, with its first partial derivatives, in G and satisfies for every sphere in G the condition

$$\lim_{R \rightarrow 0} \frac{1}{4\pi R} \int_S \frac{\partial u}{\partial R} d\Omega = cu(P) \quad (6.3)$$

then u satisfies at every point of G the equation

$$\nabla^2 u - 3c u = 0$$

In conclusion, I wish to acknowledge my indebtedness to Prof B S Madhava Rao for drawing my attention to the problem and for kind guidance.

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A REMARK ON $g(n)$.

BY S CHOWLA

(Government College, Lahore)

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PILLAI* proved that, for $n > n_0$,

$$(1) \quad g(n) = 2^n + \left[\left(\frac{3}{2} \right)^n \right] - 2$$

provided

$$2^n = l \cdot 2^r + r \quad (0 < r < 2^n) \text{ where } r > 2^n - (l + 3)$$

By combining this with a recent theorem of Mahler (*Acta arithmetica*, Band 3, p 93, Theorem 4) we obtain the result

THEOREM *Let A be an arbitrarily large number. Then there exist infinitely many x such that (1) is true for $x \leq n \leq Ax$*

Another form is the following

THEOREM *Let ϵ be an arbitrarily small positive number, then there exist infinitely many x such that the number of values of n for which $2 \leq n \leq x$ and in addition (1) is true, is less than ϵx*

(All letters, except ϵ , denote positive integers)

In fact if we denote by $K(x)$, the number of solutions of

$$1 \leq n \leq x \quad \left. \vphantom{\begin{matrix} 1 \leq n \leq x \end{matrix}} \right\} \\ g(n) = 2^n + \left[\left(\frac{3}{2} \right)^n \right] - 2$$

the above results can be put elegantly in the following form.

THEOREM

$$\lim_{x \rightarrow \infty} \sup \frac{K(x)}{x} = 1$$

Pillai proved that

$$\frac{K(x)}{x} > \frac{1}{4} \quad (x > x_0)$$

* *Annamalai University Journal*, March 1936, 5, No 2. The result mentioned was also proved by Dickson.

ON AN INFINITE SYSTEM OF NON-LINEAR INTEGRAL EQUATIONS.

BY S MINAKSHI SUNDARAM

(Madras University)

Received September 5, 1938

(Communicated by Dr R Vaidyanathanaswamy, M A., D Sc)

1 THE aim of this note is to solve the infinite system of Non-Linear Integral equations

$$(1) \quad y_n(x) = \int_0^x K_n(x, t) F_n(t, y_1(t), y_2(t)) dt$$

$$n = 1, 2, 3,$$

so that the functions $[y_n(t)]$ may belong to Hilbert Space that is to say, the series $\sum_{n=1}^{\infty} [y_n(t)]^2$ may be convergent uniformly for all values of t in a definite interval. If the functions $F_n(t, x_1, x_2, \dots)$ are all analytic in the infinity of variables x_1, x_2, \dots and continuous with respect to the variable t , we can solve the system (1) so that $\sum_{n=1}^{\infty} y_n(t)$ is absolutely and uniformly convergent, with suitable hypothesis. The general theory of such equations had been developed by Dr M R Siddiqui in a series of extension lectures given by him to the Lucknow University in January 1938, which are being published. But it is shown here that we can solve (1) uniquely with the more general hypothesis that the functions F_n are uniformly continuous with respect to all the variables and satisfy Lipschitz condition. The solution is got by method of successive approximations.

2 Our attempt is to solve the system (1), where x lies in the interval $0 < x < T$, such that for all values of x in the interval, the series

$$(2) \quad \sum_{n=1}^{\infty} [y_n(x)]^2$$

may be uniformly convergent. We assume that the functions $F_n(t, x_1, x_2, \dots)$ are, for all values of t in the interval and all real values of x_1, x_2, \dots belonging to Hilbert Space, continuous and satisfy Lipschitz's condition

$$(3) \quad [F_n(t, x_1, x_2, \dots) - F_n(t, x_1', x_2', \dots)]^2$$

$$< l_n^2 \sum_{i=1}^{\infty} (x_i - x_i')^2$$

where l_n is a positive constant, such that

$$(4) \quad \sum_{n=1}^{\infty} l_n^2 \int_0^x [K_n(x, t)]^2 dt < a$$

where 'a' is a constant independent of x . We further assume

$$(5) \quad F_n(t, 0, 0, \dots) \neq 0 \quad n = 1, 2, \dots$$

$$(6) \quad \sum_{n=1}^{\infty} \left(\int_0^x K_n(x, t) F_n(t, 0, \dots) dt \right)^2 < b$$

where b is a constant independent of x .

We now solve the system (1) by the method of successive approximations. For this purpose, we write

$$(7) \quad \begin{cases} y_n^0 = 0 \\ y_n^m(x) = \int_0^x K_n(x, t) F_n[t, y_1^{m-1}(t), y_2^{m-1}(t), \dots] dt \end{cases} \quad m = 1, 2, \dots$$

We prove that the systems (y_n^m) approximate to (y_n) so that

$$(8) \quad \lim_{m \rightarrow \infty} \sum_{n=1}^{\infty} (y_n^m)^2 = \sum_{n=1}^{\infty} (y_n)^2$$

and thus solve (1) completely. We write

$$(9) \quad \begin{cases} \chi_n^2(x) = \sum_{n=1}^{\infty} (y_n^m - y_n^{m-1})^2 \\ \chi_1^2(x) = \sum_{n=1}^{\infty} (y_n^1)^2 < b \end{cases}$$

Now from (7)

$$y_n^{m+1} - y_n^m = \int_0^x K_n(x, t) [F_n(t, y_1^m(t), y_2^m(t), \dots) - F_n(t, y_1^{m-1}(t), y_2^{m-1}(t), \dots)] dt$$

and so

$$(10) \quad (y_n^{m+1} - y_n^m)^2 \leq l_n^2 \int_0^x [K_n(x, t)]^2 dt \int_0^x \chi_m^2(t) dt$$

on account of Schwarz's inequality and (3). Summing from $n = 1$ to ∞ we observe

$$(11) \quad \begin{aligned} \chi_{m+1}^2(x) &< a \int_0^x \chi_m^2(t) dt \\ &< \frac{a^{m+1}}{\Gamma(m+1)} \int_0^x (x-t)^m \chi_1^2(t) dt \\ &< \frac{b a^{m+1} x^{m+1}}{\Gamma(m+2)} \end{aligned}$$

by induction and by (9) From (10) and (11) we at once observe that

$\sum_{n=0}^{\infty} (y_n^{m+1} - y_n^m)$ is absolutely and uniformly convergent in $(0, T)$, so that,

$$(12) \quad \lim_{m \rightarrow \infty} y_n^m = y_n$$

exists uniformly for all x in $(0, T)$. To prove that the systems (y_n^m) and (y_n) belong to Hilbert Space, we observe as in (10) and (11)

$$(13) \quad \sum_{n=1}^{\infty} (y_n^{m+1} - y_n^1)^2 \leq a \int_0^x \sum_{n=1}^{\infty} [y_n^m(t)]^2 dt$$

$$\begin{aligned} \text{Now} \quad \sum_{n=1}^{\infty} (y_n^{m+1})^2 &= \sum_{n=1}^{\infty} [y_n^1 + (y_n^{m+1} - y_n^1)]^2 \\ &\leq 2 \sum_{n=1}^{\infty} (y_n^1)^2 + 2 \sum_{n=1}^{\infty} (y_n^{m+1} - y_n^1)^2 \end{aligned}$$

and so

$$(14) \quad \sum_{n=1}^{\infty} [y_n^{m+1}(x)]^2 \leq 2b + 2a \int_0^x \sum_{n=1}^{\infty} [y_n^m(t)]^2 dt$$

Here also by induction we have

$$(15) \quad \sum_{n=1}^{\infty} [y_n^{m+1}(x)]^2 \leq 2b + 2^2 b a x + \frac{2^{m+1} b a^m x^m}{m!} < 2b e^{2ax}$$

(15) clearly shows that $\sum_{n=1}^{\infty} (y_n^{m+1})^2$ is uniformly bounded for all values of x in $(0, T)$ and all values of m . Therefore $\sum_{n=1}^{\infty} y_n^2$ is convergent for all values of x in $(0, T)$.

To prove (8) we put

$$(16) \quad {}_p R_m(x) = \sum_{n=1}^{\infty} (y_n^{m+p} - y_n^m)^2$$

and observe as in (11)

$$\begin{aligned} (17) \quad {}_p R_m(x) &\leq a \int_0^x {}_p R_{m-1}(t) dt \\ &\leq \frac{a^m}{\Gamma(m)} \int_0^x (x-t)^{m-1} {}_p R_0(t) dt \end{aligned}$$

Now from (15),

$$(18) \quad {}_p R_0(x) = \sum_{n=1}^{\infty} [y_n^p(x)]^2 \leq 2b e^{2ax}$$

and therefore (17) shows that

$$\begin{aligned}
 (19) \quad {}_p R_m &\leq \frac{2ba^m}{\Gamma(m)} \int_0^x (x-t)^{m-1} e^{2at} dt \\
 &\leq \frac{2ba^m e^{2ax}}{\Gamma(m)} \int_0^x (x-t)^{m-1} dt \\
 &= \frac{2b(ax)^m e^{2ax}}{\Gamma(m+1)}
 \end{aligned}$$

since e^{2at} is an increasing function of t . The right side of (19) is independent of p and therefore for all values of p and all values of x in $(0, T)$

$$(20) \quad \lim_{m \rightarrow \infty} {}_p R_m = 0$$

which proves (8). We have yet to show that the functions $y_n(x)$ satisfy (1). This is equivalent to proving

$$\begin{aligned}
 (21) \quad \lim_{m \rightarrow \infty} \int_0^x K_n(t, y_1^m, y_2^m) dt \\
 = \int_0^x K_n(x, t) F_n(t, y_1, y_2) dt
 \end{aligned}$$

This follows immediately on account of (20) or (8). In fact

$$\begin{aligned}
 &\left[\int_0^x K_n(x, t) \left\{ F_n(t, y_1(t), y_2(t)) - F_n(t, y_1^m(t), y_2^m(t)) \right\} dt \right]^2 \\
 &\leq l_n^2 \int_0^x [K_n(x, t)]^2 dt \int_0^x \sum_{n=1}^{\infty} (y_n^m - y_n)^2 dt
 \end{aligned}$$

and the right side tends to zero as $m \rightarrow \infty$, for every n .

3. We shall now prove that the solution thus obtained is unique. Let us suppose that there exists another set of solutions $[z_n(x)]$ satisfying (1) identically, so that

$$(22) \quad \sum_{n=1}^{\infty} (z_n)^2 < c$$

where c is a constant independent of x . Write

$$(23) \quad \begin{cases} A_m = \sum_{n=1}^{\infty} (y_n^m - y_n)^2 \\ B_m = \sum_{n=1}^{\infty} (y_n^m - z_n)^2 \end{cases}$$

then

$$(24) \quad \sum_{n=1}^{\infty} (y_n - z_n)^2 < 2A_m + 2B_m.$$

As in (10) we will have

$$(25) \quad B_m \leq a \int_0^x B_{m-1}(t) dt \leq \frac{a^{m+1}}{\Gamma(m+1)} \int_0^x (x-t)^m B_0(t) dt \\ \leq \frac{ca^{m+1} x^{m+1}}{\Gamma(m+2)}$$

where $B_0(x) = \sum_{n=1}^{\infty} z_n^2 < c$, (25) shows that

$$(26) \quad \lim_{m \rightarrow \infty} B_m = 0 \quad \text{Also} \quad \lim_{m \rightarrow \infty} A_m = 0$$

Hence from (24), letting $m \rightarrow \infty$ there

$$(27) \quad \sum_{n=1}^{\infty} (y_n - z_n)^2 = 0$$

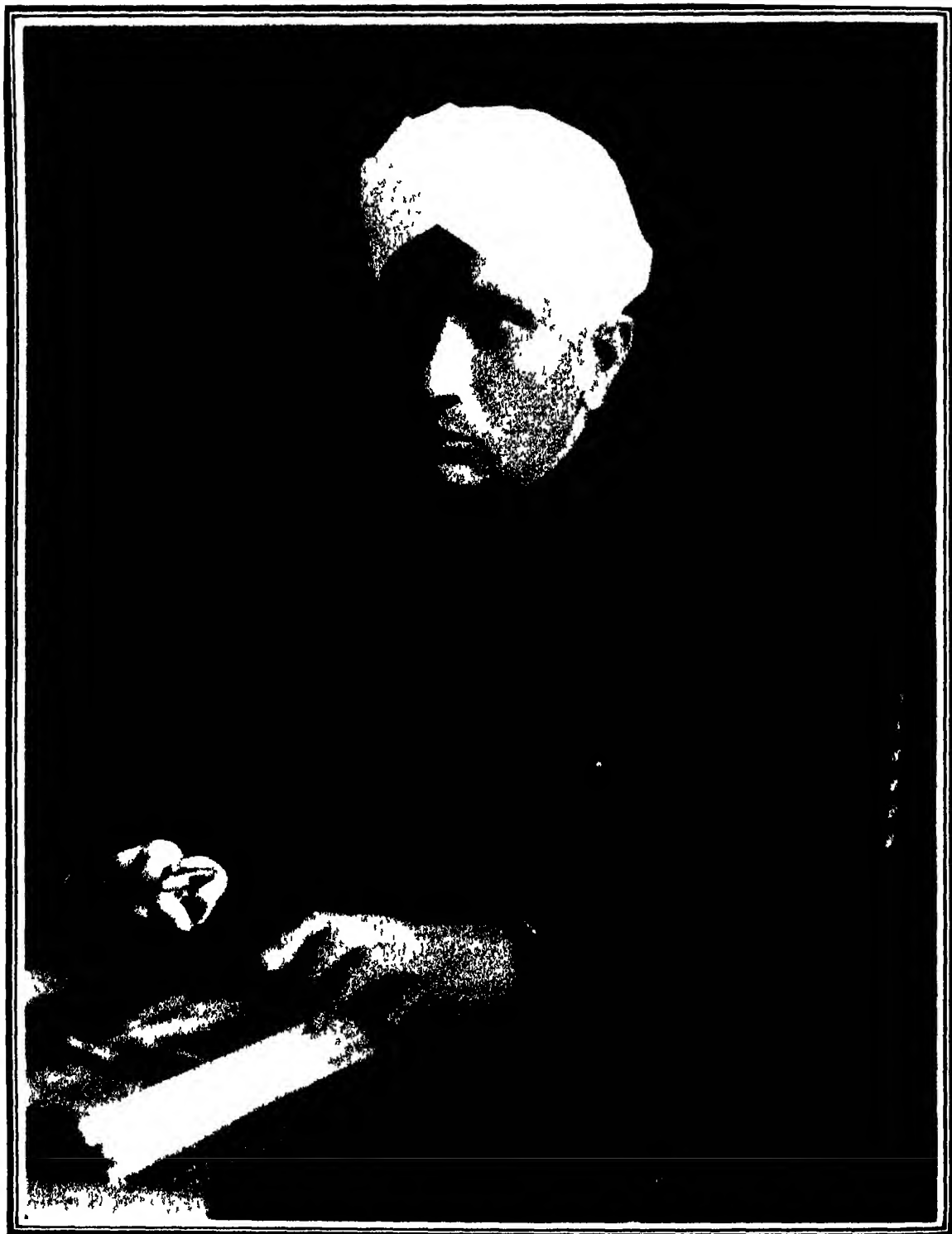
This proves that $y_n = z_n$, for every n

Finally I wish to express my sense of thankfulness to Dr M R Siddiqui for his kind criticisms in the course of preparing this paper

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C. V. Raman

SIR C. V. RAMAN'S FIFTIETH BIRTHDAY.

I

THE present issue of the *Proceedings* is a volume containing specially invited papers, which is being published by the Indian Academy of Sciences as a tribute of respect and affection to Professor Sir C V Raman on his fiftieth birthday. He is the outstanding figure in the renaissance of science which has been taking place in India during the last quarter of a century, and indeed with truth he may be designated as the creator and leader of that renaissance. The progressive enthusiasm for scientific studies and research which is witnessed on all sides in India to-day has largely been inspired by him and encouraged and sustained by his efforts. The personal example of his dedication to a scientific career, the brilliance and originality of his researches, the international character of the recognition which his work has received, his success as a teacher in training investigators who are now themselves guiding schools of research, his gift of eloquence which has served to stimulate a wide-spread interest in science, his achievements as a scientific administrator in creating facilities for research and establishing new schools of science, and his success in founding journals for publication of scientific work in India, are among the factors which have profoundly influenced the progress of science in the country. It is therefore only fitting that the occasion of his reaching half the allotted span of human life should be signalised in a manner worthy of his great work. It seems also appropriate that the contributions appearing in this volume should be prefaced by a brief account of the life and work of the leader whom they are intended to honour.

II.

Chandrasekhara Venkata Raman was born at Trichinopoly in Southern India on the seventh of November 1888. He received his early education at the Hindu College, Vizagapatam, where his father was himself a Professor of Mathematics and Physics. Later, he studied for four years at the Presidency College, Madras. From this institution, he graduated at the early age of sixteen, and two years later took his Master's degree, in both the cases with the highest distinctions. Even as an undergraduate at the Presidency College, young Raman displayed his genius for original research and independently carried out his earliest investigations in optics and acoustics which found publication in *Nature* and the *Philosophical Magazine* in 1906.

As in those days there was no scientific career open to any ambitious young Indian, Raman sat for a competitive examination held by the Government of India, and securing the highest position in it, was appointed as a Gazetted Officer of the Indian Finance Department when barely nineteen years of age

From June 1907 to July 1917, Raman served with marked distinction as an official of the Government of India, for the major part of which period he was stationed at Calcutta. During these years he continued his scientific investigations without intermission and published some thirty original communications in *Nature*, the *Philosophical Magazine* and the *Physical Review*. The capacity for scientific research thus displayed even in unfavourable circumstances greatly impressed academic circles at Calcutta, and led to his being invited by the late Sir Asutosh Mookerjee, the gifted Vice-Chancellor of the University of Calcutta, to accept the Chair of Physics newly endowed by Tarakanath Palit, a wealthy lawyer of the City. With rare courage, Raman decided to accept the offer, sacrificing a secure and lucrative official position in favour of the comparative poverty of a professorship, in order to be able to devote his whole time to science. Besides filling the Palit Chair for the next sixteen years, he also held the honorary office of Secretary of the Indian Association for the Cultivation of Science at Calcutta, in the laboratory of which the largest part of his researches for quarter of a century was accomplished. In April 1933, Raman left the Calcutta University and accepted a call from the Indian Institute of Science at Bangalore in Southern India where he now works.

III

The majority of investigators are individualists by nature, but a few are born leaders. Sir C. V. Raman belongs to the latter category. Impressive though his own personal contributions to science have been, his greater achievement is the work he has done in inspiring a whole group of investigators and creating a distinctive school of research in India. During the past twenty years, well over a hundred young men—mathematicians, physicists, chemists and geologists—have been personally initiated into research by him. These young men have been drawn to his laboratories from all parts of India, and they have been encouraged to engage in independent research and to put forth their own individual efforts with just the right kind of stimulus and assistance from their teacher. This policy has proved remarkably successful in bringing out their highest qualities and securing for them academic distinctions. The investigators who have emerged from Raman's laboratory have generally proved themselves of the very best type—brilliant, self-reliant, devoted to science, and not sparing themselves in its service. They occupy high positions everywhere in India.

and Burma, in the Professorial and teaching staff of the Universities and Colleges, and in the scientific services of the Government, and they have more than held their own in comparison with the products of foreign research schools. Much valuable scientific work is being done in India to-day by Raman's former students not only in pure physics, but also in its applications such as meteorology, seismology and soil physics. Not a few of them are pursuing the lines of research which were first initiated by Professor Raman in his laboratory. Prof. Raman's contribution towards the promotion of scientific research in India extends far beyond the circle of those who have been privileged to be his pupils or colleagues. A perusal of the scientific literature emerging from India during this period will reveal the profound influence exerted by this great leader on the work and outlook of his contemporaries. To the younger generation of scientists, he has been the leading light and a living source of inspiration.

IV

One of the ambitions of Sir Venkata Raman has been to secure a prominent place for India on the scientific map of the world. As a step forward, he realised that opportunities should be created in the country which would provide competent investigators, trained in India or elsewhere, with scientific careers, for the furtherance of their researches. Accordingly, it has been his ceaseless endeavour to create independent schools of research all over the country, to stimulate interest for research of a high standard in the Universities and the scientific institutions, and to staff them with men of proved ability in research. On this task he brought to bear his varied gifts, including his academic knowledge and experience and a grasp of financial and administrative questions such as few scientific investigators possess. There is scarcely an institution devoted to scientific research to-day in India which Sir C. V. Raman has not at some time or other actively influenced for its good. The Indian Association for the Cultivation of Science owes to his administration, the permanently endowed professorship of physics now held by one of his most distinguished pupils, a well-equipped research laboratory, a fine library, and a substantial annual grant from the Government of India which enables its work to be carried on. At the University College of Science, Calcutta, he has left a staff largely composed of his former pupils and collaborators, a finely equipped department of physics, and a great tradition for his chair to be maintained by his successors. He has taken a very special interest in the welfare of the Andhra University and played an active part in the development of the University College of Science and Technology at Waltair, which is one of the youngest and most promising centres of research in India to-day. Space does not permit of more than a passing reference to

what he has done to foster the growth of schools of research at the numerous newly founded universities in India, in nearly all of which his former pupils and collaborators are now engaged in teaching and research. One must not, however, pass over in silence the magnificent work Sir C. V. Raman has accomplished at Bangalore, where he has built up in a short time and at a minimum of expense, a research centre of remarkable efficiency which has already to its credit a notable record of scientific achievement.

V

With the rapid increase in the volume of research work in fundamental sciences in India, the need for a periodical was keenly felt and was partially met by the issues of *Bulletins* and later of the *Proceedings of the Indian Association for the Cultivation of Science* by Sir C. V. Raman. From 1926 onwards, this periodical was issued under the name of the *Indian Journal of Physics* and contained the greater part of the research work of Indian Physicists, mostly of its founder Sir C. V. Raman and his students. On his shifting from Calcutta to Bangalore in 1933, Prof. Raman found it difficult to edit the Journal and personally to supervise and strive to maintain a high standard for its publications from at a distance, and he was therefore obliged to transfer its control to the men at the spot. At the same time, the creation of an active centre of research under his direction with a band of enthusiastic young men at Bangalore, and the increased productivity in research in many of the younger Universities in India prompted him to start the Indian Academy of Sciences in 1934, with the triple object of providing a regular medium for the publication of approved papers, a platform for discussion of scientific communications, and a society for the co-ordination of scientific and industrial researches in India. Under his fostering care, the Indian Academy has, in the course of the past four years, more than justified its creation. In its *Proceedings* which are issued promptly at the end of every month, it has provided a medium in which more than half of the scientific work done in India to-day is being regularly published.

VI

The world has not been slow to recognise the importance of the achievements of Sir C. V. Raman as an investigator and a leader of scientific research. Scarcely had he completed six years as a Professor of Physics when the Royal Society of London elected him as its Fellow in 1924. He was knighted by the British Government in 1929. He was the recipient of the Matteucci Medal of the Italian Society of Sciences in 1928, of the Hughes Medal of the Royal Society in 1930, and in the same year he was awarded the Nobel Prize for Physics. He has received *honoris causa* the D.Sc. degree of the Paris

University, the LL D degree of Glasgow and the Ph D degree from Freiburg. The Universities of Calcutta, Bombay, Madras, Benares and Dacca in India have also conferred honorary doctorates on him. He is an honorary Fellow or Member of various learned societies, including especially the Royal Philosophical Society of Glasgow, the Zurich Physical Society, the Royal Irish Academy, the Deutsche Akademie of Munich and the Hungarian Academy of Sciences. He is also an honorary member of the Indian Mathematical and Chemical Societies, of the Indian Science Congress and other societies in India. He also holds an honorary Professorship at the Hindu University of Benares and at the Andhra University, Waltair.

VII

A remarkable fact about the life of Sir C. V. Raman is that he started his career as an investigator without any external stimulus and attained the greatest eminence as a scientist, by his own individual effort, sustained by the work of his devoted pupils. The fact that he had no training in foreign laboratories endowed him with a power born from within and an originality in moulding the career of young men. In later years, his ripe experience as a scientific leader was enriched by his frequent travels outside India which have afforded him opportunities of visiting the leading research laboratories and of cultivating personal relations with the leaders of Europe and America. His first visit to Europe was in the summer months of 1921, when he attended the Congress of the Universities of the British Empire held at Oxford. In 1924 he was invited to Great Britain to join the British Association for the Advancement of Science in a tour across Canada, and was requested to open a discussion on the Scattering of Light at the Toronto meeting of the British Association and of the International Congress of Mathematicians. Following this meeting, Raman visited the United States to represent India at the Centenary of the Franklin Institute at Philadelphia. At the invitation of R. A. Millikan, he spent four months at Pasadena as a Visiting Professor at the California Institute of Technology, before returning to India early in 1925. In the autumn of 1925, Raman again visited Europe as the guest of the Russian Academy of Sciences to represent India at the Bicentenary celebrations of the Academy in Leningrad and Moscow. In 1929, Raman was invited by the Faraday Society to open a discussion on molecular spectra at Bristol, and took the opportunity of visiting and lecturing at many centres of learning in Europe. He subsequently visited Europe in the winter of 1930 to receive the Nobel Prize at Stockholm, in 1932, to receive the honorary Doctorate at Paris, and in 1937, as an invitee to take part in the International Congresses of Physics at Paris and Bologna.

VIII

Sir C V Raman is entering on his fifty-first year filled with youthful energy, a buoyant enthusiasm and a single-minded devotion to the cause of science. All his friends and admirers join in wishing him health and strength to carry on his work with unabated vigour and look forward to further notable achievements by him in the field of science.

B S M.

C S V

PREFATORY NOTE TO THE SPECIAL NUMBER.

THE research papers published in the last twenty years by Sir C V Raman and the collaborators in his laboratory during the period of his Professorship include over 600 titles, and the topics with which they deal indicate an astonishing catholicity of scientific interests. The investigations concern themselves with subjects so diverse as the dynamics of vibrations and sound, the theory of musical instruments, special diffraction problems, meteorological and colloid optics, X-ray diffraction in liquids and solids, magnetism and magne-crystallic action, electro and magneto-optics, photo-elasticity of solids and fluids, dielectric behaviour, and ultra-sonics. In all of these subjects, the researches of the school have notably influenced current progress. It is not possible within any reasonable limits of space to review them even in broad outline.

By far the best-known work of Sir C V Raman is his discovery early in 1928 of the new radiation effect known by his name and which was the natural culmination of the investigations on the scattering of light systematically carried on in his laboratory since 1921. The ten years which have elapsed since the discovery of the effect have witnessed the fulfilment of the confidently expressed hope of the discoverer that it would throw new light on many problems in Physics and Chemistry. A great volume of literature has grown up round the subject, but the possibilities of further advance are as great as ever in respect of both the physical and chemical applications.

The Council of the Academy felt that it would be desirable in some way to signalise the completion of ten years' international collaboration and research on the Raman effect. Accordingly, in inviting contributions to this Special Number, they indicated the scattering of light, the Raman effect and related topics as the preferred subject. To the several distinguished contributors from outside India who have generously responded to the invitation to contribute to these *Proceedings* in spite of the very short notice given and who have helped to make this Special Number a truly international effort, the Council of the Academy tender their grateful thanks. In honouring Sir C V Raman and the Academy by their contributions, the authors have also helped to advance the cause of science, for there can be little doubt that the perusal of the contents of this volume will inspire new efforts in this field of research in many countries.

Messages conveying good wishes and felicitations have been received from many distinguished men of science including the contributors to the

volume, as also several others who owing to shortness of notice or other cause were unable to send formal papers, namely Professors C G Darwin, W Heisenberg, G Mie, W Pauli, J C Slater, A Sommerfeld and H C Urey. Professor K W F Kohlrausch of Graz, besides forwarding ten original contributions which appear in this volume, has sent a message which is reproduced below

B S M.

SEHR GEEHRTER HERR,

Anliegend finden Sie zehn Arbeiten aus dem Gebiete des " Raman-Effektes ", die das Physikalische Institut der Technischen Hochschule Graz als kleinen Beitrag zu dem Sir Venkata Raman gewidmeten Festband der " Proceedings " zu überreichen die Ehre hat

Im Dezember 1928 wurden an diesem Institute die ersten Raman-Spektren aufgenommen, die damals in Betrieb gesetzte Apparatur hat bis heute 2775, die übrigen allmählich hinzugekommenen Apparaturen haben rund 700 Aufnahmen geliefert. Die Messungs-Ergebnisse wurden in etwa 150 Publikationen verwertet, darunter waren sechs Dissertationen, drei Habilitationsschriften, zwei Bücher.

Seit 10 Jahren liegen die Arbeitsziele der Institutes fast ausschliesslich auf dem Gebiete der molekularen Schwingungsspektren, also auf einem Gebiete, das erst durch die Entdeckung des " Raman-Effektes " wirklich zugänglich gemacht wurde. Es ist kaum abzählbar, wie oft in diesen 10 Jahren der Name " Raman " ausgesprochen und wiedergeschrieben wurde.

Dass das Institut und alle seine Angehörigen jenem Manne, dessen Genie es die Möglichkeit zu diesem zehnjährigen intensiven Arbeitsbetrieb verdankt, aufrichtige Hochachtung und Verehrung entgegenbringt, ist selbstverständlich. Ich mache mich zum Sprecher aller Grazer Nütznusser seiner Entdeckung, wenn ich in ihrem und in meinem eigenem Namen Sir Venkata Raman zu seinem fünfzigsten Geburtstag auf das herrlichste beglück-wünsche.

K W. F. KOHLRAUSCH

ON THERMAL DEPENDENCE OF ELASTICITY IN SOLIDS.

BY LÉON BRILLOUIN

(Professeur au Collège de France, Président de la Société Française de Physique)

(From the Department of Theoretical Physics, College De France)

I AM very much pleased to seize the opportunity of this Jubilee Volume to pay my tribute of admiration for the wonderful work of your President, Sir Venkata Raman, whom I am glad to count among my personal friends since a good many years. Knowing the keen interest Sir Raman always brought to the problems of solid and liquid structure, I would like to present a few remarks on this very old question of physics, for old physics often wants thinking over again.

While writing last year¹ a book on elasticity and explaining the rôle of thermal agitation in solids, I tried to give a fairly logical and systematic deduction of the theory of specific heat and thermal expansion of solids, which obliged me to make some changes and improvements on the generally admitted theoretical scheme.

This brought me once more to a problem which troubled me for a long time, and where I always felt some link was missing in the reasonings, namely, how should temperature modify the elasticity coefficients of a solid body? A good many papers were written on the subject, also books and handbook-articles, but I suddenly discovered where the error was: everybody (including myself) started with a study of thermal agitation in an isotropic solid, thus analysing thermal motion into elastic waves of the two classical longitudinal and transversal types. Then, having analysed thermal agitation only for an isotropic solid, one used to take the resulting formulæ as always valid for a solid body distorted by any sort of stresses, and to build up a general thermodynamical theory of solid bodies on such a basis.

But the whole method is wrong, from a study strictly limited to isotropic solid structure, one is entitled to draw conclusions only so long as the solid remains isotropic, but nothing can be said about what happens when the solid becomes anisotropic due to the action of external unsymmetrical forces.

I just noticed this point in my book (pp 344, 345), and had to wait until recently to be able to put these general remarks into a more precise form.

¹ Brillouin, L., *Les tenseurs en mécanique et en élasticité*, Masson, Paris, 1937, Ch. XII.

I performed all necessary calculations, which are rather tiresome, but entirely justify my point of view. Let us take an isotropic solid body, then stretch this solid along the x direction, by applying X forces, the solid is now becoming anisotropic, its elastical properties along the x direction differ from those along the y or z direction, it has taken the symmetry of an uniaxial crystal. As a matter of fact, calculation checks this prediction, and shows that elastic waves propagate in such a stretched solid body in a very particular way, there are no more longitudinal and transversal waves, but for each direction of propagation one finds three different orthogonal polarisations, one of which is nearly longitudinal, the second one exactly transversal and the third one perpendicular to the first two and nearly transversal, to these three independent polarisations there correspond three different elastic wave-velocities.

Having thus obtained a rigorous analysis of thermal agitation in a strained solid body, it is possible to develop the whole thermodynamics of solids and to draw conclusions as to the influence of temperature on elasticity coefficients. The general results are as follows —

First — One may consider the elasticity coefficients which rule propagation of *hypersonic waves*, whose frequencies are near the Debye limit, those elasticity coefficients are given by the derivatives of the elastical potential energy and will be only affected in an indirect way by the thermal expansion they should accordingly show a slow decrease with increasing temperature.

Second come the *macroscopical elasticity* coefficients, as measured in the propagation of acoustical or supersonic waves; these coefficients are to be derived from the free energy instead of the potential energy, and are directly influenced by thermal agitation, it is rather difficult to predict the variation of the λ coefficient, but the rigidity coefficient μ should show a very peculiar decrease with increasing temperature. While rather slow at very low temperature, this decrease should become faster and faster at high temperature, for room temperature, and for solids not too near their melting points, the decrease might be of the order of 50 to -100 times $\frac{RT}{V}$.

Now what happens if we approach the melting point? We may by way of extrapolation guess that the macroscopical rigidity will tend to zero, while the microscopical rigidity remains finite.

While melting, the body is unable to react to shear (on macroscopical scale) but will still be able to propagate hypersonic transversal waves, so that its specific heat will remain about $3R$, just like for a solid body, and this is what really happens.

I wish to recall here an old work of Sutherland² where the following curious curve is to be found, ordinates y represent the ratio of μ (T)

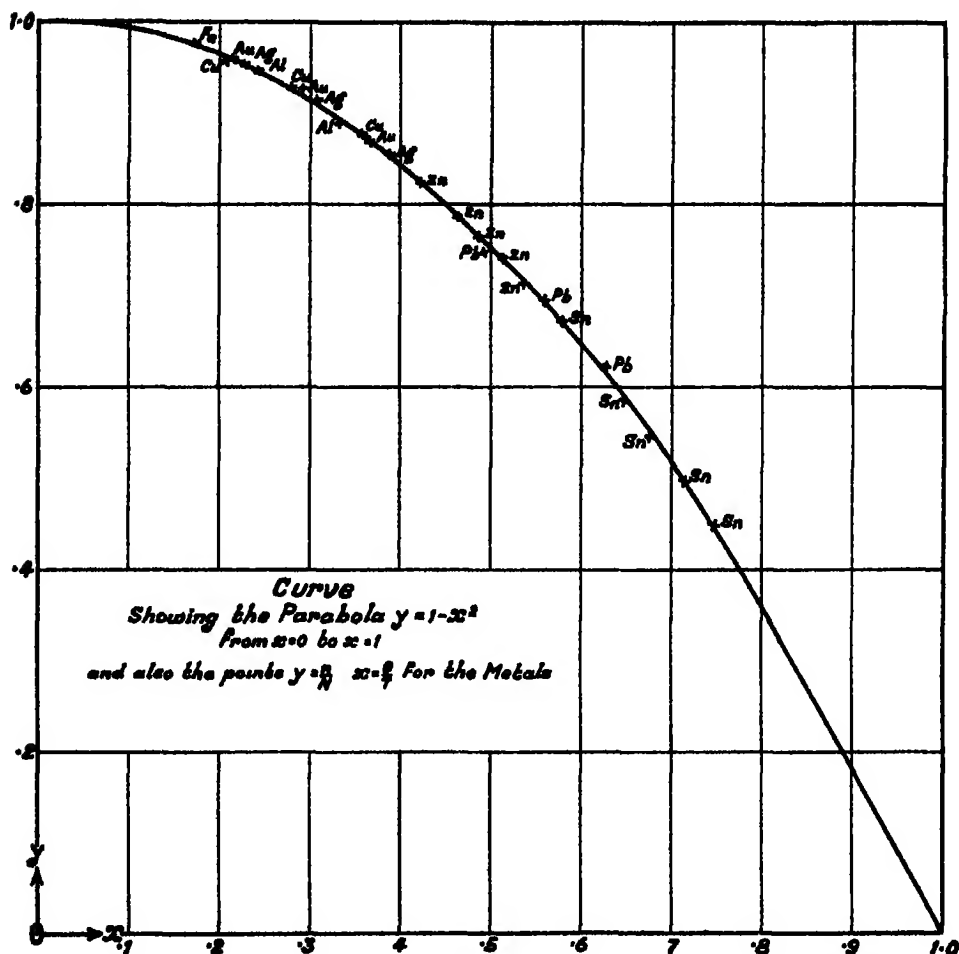


FIG 1.

to $\mu(0)$ (at zero temperature), while abscissæ x mean the ratio of absolute temperature to melting point; so that $x = 1$ is the melting point. My father repeatedly emphasized that the melting point should be defined as the point where the rigidity of a solid becomes zero; the preceding deductions seem to bring a strong support to this prediction.

Of course, it is difficult to imagine that the Sutherland curve should run smoothly up to the melting point, since it would mean melting without any

² Sutherland, *Phil. Mag.*, 1891, 32, 42.

latent heat of fusion, which is not true, but one must keep in mind the fact that the actual latent heat of fusions are always small if compared to latent heats of vaporisation, and everybody agrees now that the liquid state is often very much nearer to the solid state than to the gaseous state. Moreover, it has to be remembered that isotropic solids are but a fiction, and have been used only by way of simplification, because the complete theory of elasticity would be too complicated in case of crystals, we can guess that for a crystal the different rigidity coefficients could not tend all to zero for the same temperature, when one of these rigidity coefficients comes to zero, the whole stability of the crystal is destroyed, and this may involve a certain heat of transformation at the melting point.

The complete study, a brief account of which is here given, will appear in the "Memorial des sciences mathématiques" (Gauthier-Villars, Paris) and is now under print. I thought it worthwhile to summarize here the main results, because they suggest experimental work to be tried on solids.

- 1 Experimental determination of elasticity coefficients of solids, as functions of temperature, up to the melting point, in order to check the validity of curves of the Sutherland type—The measurements should better be carried on by ultrasonic methods.

- 2 Optical determination of the nature of hypersonic elastic waves representing thermal agitation in solids and liquids, both sides of the melting point, in order to see whether hypersonic transversal waves disappear suddenly at the melting point, or rather persist in the liquid above the melting point, as suggested here, the transversal elastic waves should presumably change progressively into transversal viscosity waves, as investigated by Lucas.

This study could be performed by means of optical determination of the structure of the Rayleigh scattered light, along the lines of the theory I developed about 1920, and of which Sir C. V. Raman himself has brought recently³ some very remarkable experimental proofs.

³ Raman, C. V., and Venkateswaran, C. S., *Nature*, August 6, 1938.

STUDIEN ZUM RAMAN-EFFEKT.

Mitteilung LXXXIX: Aethylenoxyd.

VON K W F KOHLRAUSCH

UND

A W REITZ

(174, Mitteilung aus dem physikalischen Institut der Technischen Hochschule Graz)

(Mit 3 Figuren im Text)

Es werden Beobachtungen über das Ramanspektrum des Aethylenoxyds und dessen Polarisations-Verhältnisse mitgeteilt. In der Diskussion werden die bisherigen Deutungen des Spektrums besprochen. Gegen sie wird eingewendet, daß sie erstens den experimentell bestimmten Polarisations- und Absorptions-Verhältnissen, zweitens gewissen an die innere Widerspruchsfreiheit des Deutungs-Ergebnisses zu stellenden Forderungen und drittens der Koppelungswirkung zwischen Ketten- und gleichrassigen (H-Frequenzen nicht Rechnung tragen.

Mit dem Schwingungs-Spektrum des ringförmigen Aethylenoxyds C_2H_4O haben sich bereits mehrere Autoren beschäftigt. Ueber das Ramanspektrum berichteten Lespieau-Grédy,¹ Timm-Mecke,² Ananthakrishnan,³ Bonner,⁴ über seine Polarisationsverhältnisse Ananthakrishnan,³ über das Ultrarot-spektrum Bonner,⁴ über Ramanspektren von Derivaten des Aethylenoxydes Lespieau-Grédy.¹ Versuche zur Zuordnung der Kettenfrequenzen und zur Berechnung der Molekülkonstanten (Federkräfte, Valenzwinkel) findet man bei Pai,⁵ Timm-Mecke,² Ananthakrishnan³ und Bonner.⁶ Bei der Zusammenstellung⁷ des experimentellen Befundes und bei der Sichtung der Diskussions-Ergebnisse zeigten sich gewisse Unstimmigkeiten. Mit Rücksicht auf das grundsätzliche Interesse, dass die Spektren der einfach gebauten Moleküle und besonders die der wenigen Vertreter von Ringmolekülen mit niedriger Gliederzahl haben, schien es uns der Mühe wert, den vorliegenden Fall nochmals experimentell zu bearbeiten und die Gesamtergebnisse neu zu diskutieren. In experimenteller Hinsicht schien uns zur Ergänzung zweierlei

¹ R. Lespieau, B. Grédy, *C R Acad. Sci., Paris*, 1933, **196**, 390, *Bull. Soc. chim., France*, 1933, **53**, 769.

² B. Timm, R. Mecke, *Z. Physik*, 1935, **97**, 221.

³ R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1936, **4**, 82.

⁴ L. G. Bonner, *J. chem. Physics*, 1937, **5**, 704.

⁵ N. G. Pai, *Indian J. Physics*, 1934, **9**, 123.

⁶ L. G. Bonner, *J. chem. Physics*, 1937, **5**, 203.

⁷ K. W. F. Kohlrausch, Smekal-Raman-Effekt, *Erg. B, Springer*, 1938, S. 156.

notig. Erstens zu versuchen, ob nicht durch verbesserte Versuchsbedingungen ein verbessertes (vollständigeres) Raman-Spektrum zu gewinnen sei, zweitens die Polarisations-Messungen *Ananthakrishnans*, bei denen die Intensitätsverhältnisse im π - und σ -Spektrum nicht gemessen, sondern ohne Kenntnis der Gradationskurve nur subjektiv geschätzt werden, in quantitativer Weise zu wiederholen

Experimentelle Ergebnisse

Aehnlich wie die niederen Alkohole liefert auch Äthylenoxyd einen unerwartet starken Untergrund, dessen Intensität das Auffinden sehr schwacher Streulinien erschwert. Es wurde daher große Sorgfalt auf die Reinigung der Substanz gelegt (mehrfache Destillationen in der "Tiefsiede-Apparatur"), die schließlich in N_2 -Atmosphäre in das Ramanrohr übergeführt wurde. 10 Aufnahmen, 6 mit Filter, 4 ohne Filter mit variiertem Expositionszeit und mit normalem (0,06) bzw. verengertem (0,03) Spalt wurden gemacht, es wurden zwar Verbesserungen erzielt, doch nicht im Verhältnis zur aufgewendeten Mühe. Die Messungsergebnisse wurden zu einem gemittelten Streuspektrum zusammengezogen und aus den 50 Linien desselben das folgende Ramanspektrum abgeleitet (e_{10} bedeutet z. B., daß die betreffende Streulinie auf 10 Platten von Hg ϵ erregt gefunden wurde)

$\Delta\nu = 250 (00) (e_4), 417 (00) (e_2), 509 (0) (e_3), 569 (0) (e_3), 603 (00) (e_3), 704 (0) (e_3, \sim g - 805), 806 (5b) (k_4, \nu_2, + e_1, e_{10}, c_6), 863 (5b) (k_4, \nu_3, e_{10}, c_1), 1023 (0) (e_3, \sim g - 1124), 1059 (\frac{1}{2}) (e_3, \sim f - 1116); 1120 (4) (k_4, \nu_1, e_{10}), 1153 (1) (k_4, \nu_1, e_6), 1267 (10) (k_4, \nu_4, f_3, e_{10}), 1379 (0) (e_3), 1469 (0) (e_3), 1487 (1) (k_4, e_4), 2915 (8) (q_4, k_4, \nu_3, e_{10}), 2958 (7) (q_3, p_1, k_4, \nu_4, e_{10}), 3007 (10) (q_3, o_3, k_4, \nu_4, e_{10}), 3061 (2) (p_3, o_3, k_3, \nu_4, e_1)$

Die Linien 250, 417, 603, die an der Grenze der Beobachtbarkeit liegen, sowie Linie 1059 ($\frac{1}{2}$) (Ueberdeckung mit $f - 1116$) halten wir für sehr unsicher. Von den restlichen, gegenüber den bisherigen Beobachtungen neuen Linien, nämlich 509 (0), 569 (0), 704 (0), 1023 (0), 1379 (0), 1469 (0) mochten wir als zu wenig gesichert noch ausscheiden 569 und 704.

An Polarisations-Aufnahmen⁸ wurden drei durchgeführt; zwei mit Filter, und eine ohne Filter, um die von Hg ϵ erregten, im Blau gelegenen ν (CH)-Frequenzen zu erfassen. Das Ergebnis war: (Neben der Frequenz steht in Klammern die Summe der im π - und σ -Spektrum gemessenen Intensitäten, sowie deren Verhältnis ρ_{π}) 806 (54, 0,85, 0,87, 0,80), 863 (53, 0,81, 0,87, 0,77), 1123 (37, 0,21, 0,26, 0,24); 1153 (24, 0,73, 0,65,—; überdeckt durch die hoch-polarisierte Linie $f - 1267$); 1267 (177; 0,07,

⁸ Vergl. A. W. Reitz, *Z. physik. Chem.*, 1936, (B), **33**, 368; 1937, **38**, 275, 381.

0,08, 0,13); 1487 (15, 0,65, 0,58, 0,51), 2915 (79, —, —, 0,19), 2958 (70, —, —, 0,15 [$\epsilon - 1153$!]), 3007 (163, —, —, 0,11), 3061 (64, —, —, 0,80)

Endlich sei in Fig 1 die von Bonner (*loc cit*) im Bereich von 1 bis 16μ aufgenommene Absorptionskurve des gasförmigen Aethylenoxyds wiedergegeben, da aus ihr die in Tabelle 1 angeführten Absorptions-Intensitäten entnommen wurden, am Fusse der Figur wurden die beobachteten Ramanlinien eingetragen

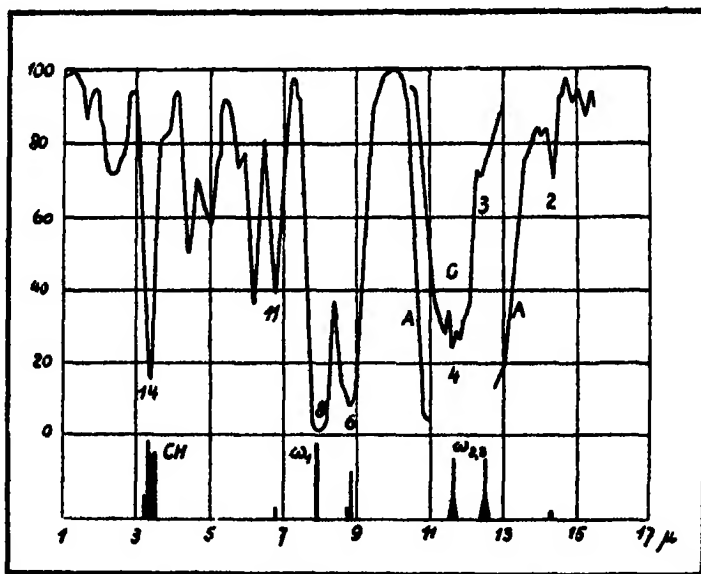


FIG. 1.

Bonner's Absorptions-Spektrum des gasförmigen Aethylenoxydes, verglichen mit dem Ramanspektrum, Abszisse Wellenlänge in μ 15 cm C_2H_4O -Gas bei 700 (Kurve A) bzw. 25 (Kurve C) mm Druck.

Die Gesamtergebnisse sind in Tabelle I zusammengestellt und bilden die experimentelle Grundlage der anschliessenden Diskussion. Zu ergänzen ist die Tabelle durch die folgenden von Bonner gefundenen, als Grundtöne aber kaum in Frage kommenden Absorptionsfrequenzen, ihre Ablesegenauigkeit und (in Klammer) ihre nach Fig 1 geschätzte Intensität sowie eine versuchsweise Erklärung: 1626 ± 5 (m, 2.813), 1733 ± 6 (s s, 2.867), 2024 ± 8 (m; $\sim 1134 + 862$); 2304 ± 10 (m, $1493 + 804$); 2632 ± 20 (s s, $1134 + 1493$); 3891 ± 40 (s, $3021 + 862$); 4130 ± 70 (s, $3021 + 1134$), 6211 ± 100 (s; $\sim 2 \cdot 3021$).

TABELLE I

Das Schwingungs-Spektrum von Aethylenoxyd

Raman Spektren						Absorption Spectre
	Lespieau Grédy	Timm Mecke	Ananthakrishnan	Bonner	K W F K A W R	Bonner
1					509 (o) ?	
2					704 (o) ?	696 \pm 3 (s s)
3	808 (6)	807 (o)	807 (8 b, dp)	807	806 (5b, dp)	804 \pm 2 (s s)
4	869 (6)	873 (1)	869 (8b, dp)	867	863 (5b, dp)	862 \pm 2 (s st PQR)
5					1023 (o ?)	
6	1119 (3)	1128 (1)	1122 (5 p)	1123	1120 (4, p)	1134 \pm 3u (t)
7			1159 (2b, dp)		1153 (1, dp)	
8	1269 (6)	1268 (5)	1270 (15, p)	1269	1267 (10, p)	1255 \pm 3 (sst, PQR)
9	.				1379 (o ?)	
10					1469 (0, dp ?)	
11			1492 (1b, dp ?)	1488	1487 (1, p)	1493 \pm 5 (m)
12	2017 (3)	2024 (1)	2017 (6, p)	2014	2015 (8, p)	
13	2059 (3)	2070 (1)	2060 (6, p)	2058	2058 (7, p)	
14	3000 (3)	3008 (1)	3008 (10, p)	3007	3007 (10, p)	3021 \pm 20 (st)
15		3047 (1)	3062 (4b, dp)	3061	3061 (2, dp)	

Zwecks Erleichterung des im Folgenden immer wieder herangezogenen Vergleiches mit den Verhältnissen bei Cyclopropan, sind in Fig 2 die Spektren der beiden Grundkörper C_2H_4 und C_2H_4O sowie die der beiden einzigen derzeit bekannten Derivate mit gleichartigen Substitution, nämlich der 1, 2-Dimethyl-Derivate eingetragen.

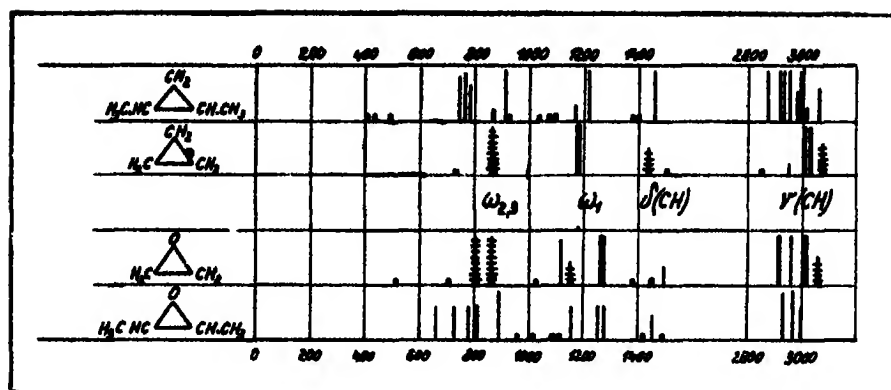


FIG 2

Die Ramanspektren von Cyclopropan und Äthylenoxyd
sowie ihrer 1, 2-Dimethyl-Derivate

Diskussion

(A) *Auswahlregeln und Schwingungsformen* Für Cyclopropan mit der Symmetrie D_{3h} gelten die Auswahlregeln der linken Hälfte von Tabelle II, die ω gehören zu Ketten—, die γ, δ, ν zu CH-Schwingungen. Wurde man eine der drei Methylengruppen des Cyclopropanes verändern, etwa $\text{CH}_3 \rightarrow \text{CD}_3$ oder $\text{C}^{13}\text{H}_3 \rightarrow \text{C}^{13}\text{H}_2$, dann wurde die Symmetrie von D_{3h} auf C_{2v} erniedrigt und man erhielt die Auswahlregeln der rechten Seite von Tabelle II. Dabei spalten die zweifach entarteten Schwingungen vom Typus E' bzw. E'' auf in solche vom Typus A_1 und B_1 bzw. vom Typus A_2 und B_2 . Ersetzt man andererseits eine CH_3 -Gruppe durch O, dann verschwinden überdies die zu ihr gehörenden δ, γ, ν (CH)-Frequenzen, die in der letzten Spalte zusammengestellt sind.

TABELLE II

Die Auswahlregeln für Cyclopropan und Äthylenoxyd.

Kette	CH		$\sigma_x \sigma_y$	Kette	CH
A_1' p ia	$\omega_1 \delta \nu$	$\begin{matrix} \nearrow \\ \searrow \end{matrix}$	A_1 s s p M_z	$\omega_2 \omega_1 \gamma_1 \delta_1 \nu_1 \delta \nu$	
E' dp M ₁	$\omega_{2,3} \gamma \delta \nu$	$\begin{matrix} \nearrow \\ \searrow \end{matrix}$	B_1 as s dp M_x	$\omega_2 \gamma_2 \delta_2 \nu_2 \gamma$	
A_2' v ia	$\gamma \cdot \cdot$	$\begin{matrix} \nearrow \\ \searrow \end{matrix}$	A_2 as as dp ia	$\gamma_3 \delta_3 \nu_3 \gamma$	
A_1'' v ia	$\gamma \cdot \cdot$	$\begin{matrix} \nearrow \\ \searrow \end{matrix}$	B_2 s as dp M_y	$\gamma_4 \delta_4 \nu_4 \delta \nu$	
E'' dp ia	$\cdot \gamma \delta \nu$	$\begin{matrix} \nearrow \\ \searrow \end{matrix}$			
A_2'' v M_y	$\cdot \cdot \delta \nu$	$\begin{matrix} \nearrow \\ \searrow \end{matrix}$			

Cyclopropan D_{3h}
A2

Äthylenoxyd C_{2v}

r

Die Schwingungsformen des Aethylenoxyds sind in Fig. 3 wiedergegeben. Ihre Bezeichnung stimmt mit der von Tabelle II überein. Zu beachten ist nur, daß für die Kettenschwingungen die σ_y , für die CH-Schwingungen jedoch zur leichteren Darstellung die σ_z -Ebene in die Papierebene gelegt wurde. Die Formen sind schematisiert und hängen noch von den dynamischen Verhältnissen des Moleküles ab.

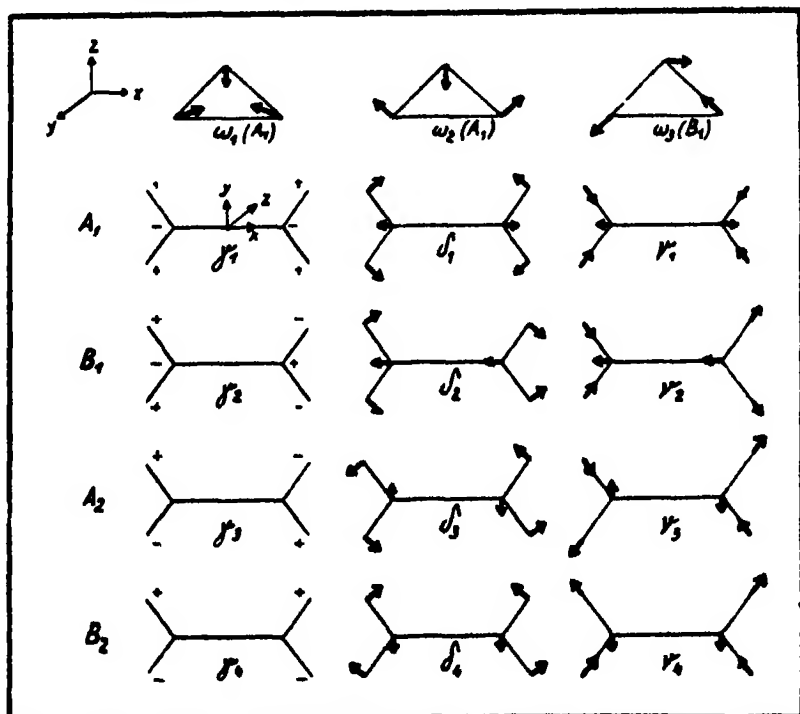


FIG. 3

Schematische Formen der Ketten- und CH-Schwingungen von Aethylenoxyd

Der summarische Vergleich zwischen der in Tabelle II enthaltenen Erwartung und der in Tabelle I zusammengestellten Beobachtung ergibt für das Ramanspektrum.

	$\nu(\text{CH})$		im Frequenzgebiet unter 1600		insgesamt	
	p	dp	p	dp	p	dp
Linienzahl erwartet	1	3	4	7	5	10
„ beobachtet	3	1	3	7-8	6	8-9

Sicher tritt demnach im Gebiet der CH-Valenzfrequenzen, ähnlich wie bei Cyclopropan,⁹ etwas unerwartetes ein. Statt nur einer polarisierten Linie werden ihrer drei gefunden. Ein Teil dieser Unstimmigkeit, vielleicht auch die ganze, wird wohl auf "Fermi-Resonanz" [$\nu(\text{CH}) \approx 2\delta(\text{CH})$, z. B. $2 \cdot 1469 = 2938$, $2 \cdot 1487 = 2974$] und die dadurch bewirkte Linienvermehrung zurückzuführen sein. Im Frequenzgebiet unter 1600 cm^{-1} ist obiger Vergleich unsicher, da—etwas willkürlich—die schwachen Linien Nr. 1, 2, 5, 9, 10, deren Polarisationszustand nicht bestimmt werden konnte, als depolarisiert eingesetzt wurden. Immerhin wird man sich wundern müssen, daß von den zu erwartenden 4 totalsymmetrischen Schwingungen, die doch meist zu kraftigen und polarisierten Linien führen, nur drei gefunden wurden.

(B) *Das Kettenpektrum des Dreiecks-Modelles*. Bezeichnet man in Cyclopropan die Federkraft für die C-C-Bindung mit f' , die Masse der Gruppe CH_2 mit m , die Deformationskonstante mit d' , dann gilt bekanntlich (S. R. E. Erg. Bd. S. 66) für ein Valenzkraftmodell

1 (a) $n_1^2 = 3f'/m$, 1 (b, c) $n_2^2 = 3(f' + 3d')/2m$, mit $n^2 = 5,86 \cdot 10^{-3} \omega^2$. Bezeichnet man beim Übergang zum Äthylenoxyd die neue CO-Federkraft mit f , die Masse von O mit M , den halben Valenzwinkel an O mit α , die Deformationskonstante für die Änderung dieses Winkels mit d , dann gilt (S. R. E. Erg. Bd., S. 65)

$$2 \text{ (a) } n_1^2 + n_2^2 = 2f'/m + f(1 + 2 \frac{m}{M} \cos^2 \alpha)/m + (2d + d')(1 + 2 \frac{m}{M} \sin^2 \alpha)/m$$

$$2 \text{ (b) } n_1^2 n_2^2 = \left(1 + 2 \frac{m}{M}\right) [2ff' \cos^2 \alpha/m^2 + 2f'(2d + d') \sin^2 \alpha/m^2 + f(2d + d')/m^2]$$

$$2 \text{ (c) } n_2^2 = (f + 4d' \cos^2 \alpha) \left(1 + 2 \frac{m}{M} \sin^2 \alpha\right)/m$$

Der wesentliche Unterschied in diesen beiden Fällen—und auf ihn wurde auch bei den bisherigen Diskussionen das Hauptgewicht gelegt—besteht also, wie ebenso aus Tabelle II hervorgeht, darin, daß bei Erniedrigung der Symmetrie von D_{3h} auf C_{2v} die entartete Schwingung ω_2 ,₂ aufspaltet in eine mit ω_1 rassengleiche totalsymmetrische (ω_2) und in eine antisymmetrische Schwingung ω_3 . Es ist für das Folgende von einigem Interesse die Größe dieser Aufspaltung in Abhängigkeit von den Modellkonstanten etwas näher zu betrachten.

Wenn man¹⁰ in Cyclopropan $f' = f = 3,85 \cdot 10^5$, $d' = d = 0,085 \cdot 10^5$, $M = m = 14$, $\alpha = 60$ setzt, erhält man aus den Formeln 1 oder 2 die mit

⁹ K. W. F. Kohlrusch und R. Skrabal, *Mh. Chem.*, 1937, 70, 377.

¹⁰ K. W. F. Kohlrusch und F. Koppl, *Z. physik. Chem.*, 1934, (B), 20, 209.

der Beobachtung übereinstimmenden Frequenzwerte

$$\omega_1 = 1186, \omega_{2,3} = 866,$$

von denen, wie es nach Tabelle II sein soll, erstere p und ia , letztere dp und a ist. Ändert man am Modell nichts anderes, als daß nun $m = 14$, $M = 16$ wird, dann erhält man aus Gl. 2)

$$\omega_1 = 1162, \omega_2 = 846, \omega_3 = 848$$

Die Frequenzen erniedrigen sich entsprechend der Änderung der schwingenden Gesamtmasse von 42 auf 44 um den Faktor $\sqrt{42/44}$, die Aufspaltung $\omega_2 - \omega_3 = 2 \text{ cm}^{-1}$ ist so gering, daß sie angesichts der ziemlichlichen Linienbreite von $\omega_{2,3}$ der Beobachtung entgehen würde. Erst wenn man die Werte der Kraftkonstanten f und f' verschieden macht oder die Gleichheit der Winkel aufhebt, kommt es zu praktisch merklichen Aufspaltungen, wie die Durchrechnung einiger Beispiele und ihr in Tabelle III zusammengestelltes Ergebnis zeigt. In dieser Tabelle unterscheiden sich die Modelle einer Horizontalreihe im wesentlichen nur in den Konstanten f und f' , die einer Kolonne nur durch die Verschiedenheit von a . Man liest aus der Tabelle ab, daß ω_1 fast unabhängig von a und (in Analogie zu Gl. 1a) im wesentlichen gegeben ist durch $n_1^2 = 3 \cdot (f' + 2f)/(2m + M)$, daß mit zunehmendem Valenz-Winkel ω_2 stets ab-, ω_3 stets zunimmt und daß die Gleichheit $\omega_2 \sim \omega_3$ im ersten Feld bei $2a = 60^\circ$, im zweiten Feld bei $2a \simeq 64^\circ$, im dritten Feld bei $2a \simeq 54^\circ$ eintritt, sie wurde im ersten Fall notwendige, in den beiden andern Fällen zufällige Entartung bedeuten.

TABELLE III

Frequenzgang für das Dreiecksmodell bei Variation der Modellkonstanten ($d = d' = 0.085$)

a	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3
24°	1186	908	819	1190	933	806	1224	910	867
27°	1185	888	841	1147	908	824	1223	890	886
30°	1186	866	866	1200	883	848	1219	871	912
33°	1184	844	893	1209	852	868	1222	844	936
36°	1186	817	917	1213	824	892	1221	819	961

$$f = f' = 3.85 \cdot 10^5 \\ m = M = 14$$

$$f = 3.85, f' = 4.5 \\ m = 14, M = 16$$

$$f = 4.5; f' = 3.85 \\ m = 14, M = 16$$

(C) *Modellmäßige Behandlung des molekularen Kettenpektrums.* Verwendet man die Formeln (2) zur Beschreibung des molekularen Kettenpektrums und macht man die plausible Annahme, daß auch in einem

gespannten System unter sonst gleichen Umständen zur größeren Federkraft die kleinere Atomdistanz gehört, dann sind von den in Tabelle III gerechneten Beispielen einige als wirklichkeitsfremd auszuschalten. Setzt man nämlich ein bestimmtes Größenverhältnis $f(\text{CO})/f'(\text{CC})$ voraus, so ist damit eine Aussage über das Verhältnis der Atomentfernungen $s(\text{CO})/s'(\text{CC})$ und daher eine Aussage über die Stumpf- oder Spitzwinkligkeit des Dreieckes verbunden, und nur jene Fälle der Tabelle III können im Molekül realisiert sein, bei denen in dieser Hinsicht kein Widerspruch besteht. In Feld I ($f = f'$, also $s = s'$) ist nur die Lösung für $2\alpha = 60^\circ$ physikalisch sinnvoll, in Feld II ($f < f'$, $s > s'$) trifft dies nur für die Lösungen mit $2\alpha < 60^\circ$, in Feld III ($f > f'$, $s < s'$) nur für die Fälle mit $2\alpha > 60^\circ$ zu.

Par (loc cit) hat die Formeln eines Zentralkraftsystemes (man setze in den Gl. 2 die Größen d und d' gleich Null) verwendet, als Kettenfrequenzen aber 810, 865, und 1123 eingesetzt, infolge der falschen Wahl für ω_1 (1123 statt 1267) scheiden seine rechnerischen Ergebnisse aus der Diskussion aus.

Ananthakrishnan (loc. cit) rechnet ebenfalls mit den Formeln des Zentralkraftsystemes und erhält als Lösungen

ω_2	ω_3	ω_1	$f'(\text{C}\cdot\text{C})\cdot 10^{-5}$	$f(\text{C}\cdot\text{O})\cdot 10^{-5}$	2α
807	869	1270	5,59	3,69	51° (1)
			3,22	4,95	22° (2)
869	807	1270	5,16	3,9	72° (3)
			3,02	5,04	44° (4)

Nr. 3 dieser Lösungen wird in Fett-Druck wiedergegeben und offenbar für die passendste gehalten. Nach dem was über den Zusammenhang zwischen f/f' und dem Valenzwinkel gesagt ist, aber nur Lösung (1) in dieser Hinsicht widerspruchsfrei; in anderer Hinsicht ist sie jedoch recht unwahrscheinlich. Denn im allgemeinen ist $s(\text{CO}) < s'(\text{CC})$ und daher ist, da man kaum annehmen wird, daß durch die Ringspannung das Größenverhältnis umgekehrt wird, ein stumpfwinkliges Dreieck mit $f(\text{CO}) > f'(\text{CC})$ zu erwarten.

Bonner (loc cit) verwendet ebenfalls das Zentralkraftsystem, führt aber Wechselwirkungsglieder $2f_{12}(\Delta s)^2 + 4f_{13}(\Delta s \Delta s')$ in das Potential ein. Die Frequenzformeln, umgeschrieben in die bei den Gl. 2) gewählte Darstellungsweise, lauten dann (mit $\rho = s'/s$)

$$3 \cdot (a) \quad n_1^2 + n_2^2 = (f + f_{12}) \left(1 + 2 \frac{m}{M} \cos^2 \alpha \right) / m + 2 (f' + f_{12} \cdot \rho) / m$$

$$3 \text{ (b) } n_1^2 n_3^2 = \left(1 + 2 \frac{m}{M}\right) (f'f + f'f_{12} - 2f_{13}^2) 2 \cos^2 \alpha / m^2$$

$$3 \text{ (c) } n_3^2 = (f - f_{12}) \left(1 + 2 \frac{m}{M} \sin^2 \alpha\right) m$$

Diese Gleichungen reduzieren sich für $f = f'$, $f_{12} = f_{13}$, $m = M$, $s' = s$, $2\alpha = 60^\circ$ auf

$$4 \text{ (a) } n_1^2 = 3(f' + 2f_{12})/m, \quad 4 \text{ (b, c) } n_2, n_3^2 = 3(f' - f_{12})/2m,$$

die ihrerseits für $f_{12} = 0$ übergehen in die Gl (1), wenn dort $d' = 0$ gesetzt wird. Für Cyclopropan ergab sich mit den Formeln (4) $f' = 4,04 \cdot 10^5$, $f_{12} = 0,085 \cdot 10^5$ Dyn/cm. Für Aethylenoxyd muß Bonner, da 5 Unbekannte ($f, f', f_{12}, f_{13}, \alpha$) nur drei bekannten Frequenzwerten ($\omega_1 = 1270$, $\omega_3 = 807$, $\omega_8 = 869$) gegenüberstehen, willkürlich vorgehen, welche Gesichtspunkte ihn leiteten, wird nicht angegeben. Seine Lösung ist $f' = 3,73$, $f = 4,43$, $f_{12} = 0,33$, $f_{13} = 0,20$, dies entspricht, wie man nachrechnet, einem Winkelwert $2\alpha \approx 64^\circ$. Hier gehört also in der Tat zu einem $f/f' > 1$ ein stumpfwinkliges Dreieck. Man kann also unter den vielen hier möglichen Lösungen auch vernünftige angeben, ohne daß von den letzteren eine im besonderen ausgezeichnet wäre. Diese überbleibende Willkür, die der Angabe von Zahlenwerten für die Molekulkonstanten den gesicherten Boden entzieht, ist bei diesem Verfahren zu bemängeln, zu bemängeln ist ferner der Umstand, daß f_{12} in Cyclopropan ($-0,085$) und Aethylenoxyd ($+0,33$) so ganz verschieden sein soll.

Ferner ist gegen die in allen besprochenen Fällen verwendete Voraussetzung, dass nämlich $\Delta\nu = 806$ der *totalsymmetrischen* Kettenfrequenz ω_2 zuzuordnen sei, der schwerwiegende Einwand zu erheben, dass die Linie 806 zweifellos ebenso depolarisiert ist wie 863. Dagegen zeigt $\Delta\nu = 806$ gegenüber der Kettenfrequenz $\omega_3 = 863$ den bemerkenswerten Unterschied, daß bei letzterer (ebenso wie in Cyclopropan) eine sehr kräftige Absorptionsstelle liegt, während bei 806 (vergl Fig 1) die ν -Absorption nur eben merklich ist. Rechnet man aber die zu ω_2 und ω_3 gehörigen Schwingungsformen und die dazugehörigen Relativwerte der Dipolmomente aus, so ist für einen derartigen starken Unterschied in der optischen Aktivität kein Hinweis zu finden. Die Schwingungen $\omega_1, \omega_2, \omega_3$ sollten vielmehr ungefähr gleich stark absorbieren.

Wir sind daher der Meinung, daß $\Delta\nu = 806$ nicht zur Kettenfrequenz ω_2 gehört, dass vielmehr Entartung vorliegt und anzusetzen ist. $\omega_2 = \omega_3 = 863$. Da nach dem zu Tabelle III am Anfang von Abschnitt C Gesagten eine solche Entartung nur für $2\alpha \approx 60^\circ$ sinnvoll ist, folgern wir $f \approx f'$, $s \approx s'$, $d \approx d'$, $2\alpha \approx 60^\circ$.

Für diesen Fall vereinfachen sich die Formeln (2) und (4), man erhält

$$5 \text{ (a) } n_1^2 = 2f \left(1 + \frac{1}{2} \frac{m}{M}\right)/m \quad 5 \text{ (b, c) } n_2^2 = n_3^2 = (f + 3d)$$

$$\left(1 + \frac{1}{2} \frac{m}{M}\right)/m$$

$$6 \text{ (a) } n_1^2 = 2(f + 2f_{12}) \left(1 + \frac{1}{2} \frac{m}{M}\right)/m, \quad 6 \text{ (b, c) } n_2^2 = n_3^2 = (f - f_{12})$$

$$\left(1 + \frac{1}{2} \frac{m}{M}\right)/m$$

Wendet man diese auf das Kettenspektrum $\omega_2 = 863$, $\omega_1 = 1267$ an, so erhält man

$$\text{nach (6) } \quad f = 4,36, \quad f_{12} = +0,112$$

$$\text{nach (5) } \quad f = 4,58, \quad d = -0,112$$

In beiden Fällen ist, wie wegen des Bindungsausgleiches zu erwarten, f größer als in Cyclopropan ($f = 4,04$ bzw. $f = 3,85 \cdot 10^6$), in beiden Fällen wechseln aber die Korrektionsglieder f_{12} bzw. d gegenüber Cyclopropan ($f_{12} = -0,085$ bzw. $d = +0,085$) das Vorzeichen, was speziell für das Valenzkraftsystem zum sinnlosen negativen d -Wert führt

Aus diesem Ergebnis darf man aber noch nicht, wie es *Bonner* tat, schließen, daß die Beschreibung der Ringspektren durch die Frequenzformeln 3, 4 und 6 den wahren Verhältnissen besser angepasst sei als die Beschreibung durch die Formeln 1, 2 und 5. Denn in beiden Fällen wurde eine zwar übliche und bequeme, aber nicht statthafte Vernachlässigung von zunächst nicht absehbarer Wirkung getroffen. Nämlich die Vernachlässigung der Kopplung zwischen gleichrassigen Ketten- und CH-Schwingungen.

Im speziellen Falle des Cyclopropanes und seiner totalsymmetrischen Schwingungen lassen sich die Verhältnisse noch halbquantitativ übersehen. Nach Tabelle II ist hier die Ketten-Schwingung $\omega_1 = 1186$ mit einer δ (CH) Schwingung (vermutlich um 1500) und einer ν (CH)-Schwingung (~ 3015) gekoppelt. Wir haben die zugehörige Frequenzgleichung¹¹ dritten Grades unter Einsetzung passender Modellkonstanten ausgewertet und folgendes Ergebnis erhalten

	ω_1	δ (CH)	ν (CH)
(a) ungekoppelt	1257	1503	2911
(b) ω_1 und δ (CH) gekoppelt	1171	1656	2911
(c) alle drei gekoppelt	1153	1625	2933

¹¹ Vergl. K. W. F. Kohlrausch und R. Seka, *Ber. Deutsch. chem. Ges.*, 1936, 69, 729

Man erkennt an diesen Zahlen, die nur relativ zu werten sind, den Einfluss der vernachlässigten Koppelung zwischen Ketten- und CH-Frequenzen. Durch die Koppelung von ω und δ werden die ungekoppelten Frequenzen ω_a und δ_a wie üblich auseinandergetrieben, ω geht nach tieferen (höheren) Werten, wenn δ_a ursprünglich höher (tiefer) lag als ω_a , die Verschiebung beider Frequenzen ist bekanntlich umso grösser je stärker die Koppelung und je näher δ_a an ω_a liegt. Kann ein System außer der ω - und δ -noch überdies eine gleichrassige hohe ν (CH)-Schwingung ausführen, dann treten die in Zeile c beschriebenen Veränderungen auf. Die enge Koppelung der CH-Schwingungen untereinander bewirkt trotz der großen Frequenzdifferenz noch ein merkliches Auseinanderrücken von δ_c und ν_c gegenüber dem nicht gekoppelten Fall δ_b und ν_b . Das Heranrücken von δ_c an ω_b bewirkt eine neuerliche Erniedrigung desselben nach ω_c .

Diese Erscheinung hat nun, mindestens was die totalsymmetrischen Frequenzen anbelangt, *qualitativ* zur Folge. Will man für Cyclopropan die vereinfachten Formeln 1 (a) oder 4 (a) anwenden, so hat man $m = 12$ zu setzen, dafür aber für ω_1 einen merklich höheren Wert als 1186 zu verwenden, denn dieser Wert ist wegen der Koppelung mit den *höheren* δ (CH)-Schwingungen sicher *zu tief*. Will man für Äthylenoxyd die Formeln 5 (a) oder 6 (a) verwenden, so hat man wieder $m = 12$ zu setzen, jetzt aber aller Wahrscheinlichkeit nach einen merklich tieferen Wert als $\omega_1 = 1267$ zu verwenden. Dann laut Tabelle II, ist jetzt ω_1 zwar wieder mit den *höheren* δ (CH)- und ν (CH)-Schwingungen (vermutlich $\delta_1 \sim 1487$, $\nu_1 \sim 3000$) gekoppelt, überdies aber mit einer *tieferen* γ (CH)-Schwingung, liegt letztere, wie nach den Polarisationsverhältnissen zu schließen ist, bei $\gamma_1 \sim 1120$, also im ungekoppelten Zustand sehr nahe an ω_1 , dann ist ihre Kopplungswirkung die stärkste und besteht in einer *Erhöhung* von ω_1 .

Wie sich diese Umstände *quantitativ* auswirken, läßt sich ohne eingehende rechnerische Behandlung nicht voraussagen, diese ist aber im Falle des Äthylenoxyds, bei dem man es mit Frequenzgleichungen höheren als dritten Grades zu tun bekommt, recht schwierig. Es scheint uns aber, als ob es der Muhe wert wäre, diese verhältnismäßig einfach gebauten Moleküle zum Gegenstand einer eingehenden theoretischen Untersuchung, zu der uns selbst Zeit und Eignung fehlt, zu machen.

LIGHT SCATTERING IN ANISOTROPIC MEDIA.

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THE discovery of the so-called Krishnan effect of light scattering by R S Krishnan in Sir C V Raman's Institute has opened a new field of experimental research and has been responsible for a new theoretical attack on the problems of light scattering by solids and liquids. It has been shown (Mueller, 1938) that Krishnan's observations can readily be explained by assuming that the scattering originates from fluctuations of the refractive properties analogous to those produced by a random distribution of standing longitudinal and transversal waves in a medium with photoelastic properties. According to this theory the Krishnan effect should exist for temperature scattering in solids and for structure scattering in glasses and liquids. It seems likely that the theory applies also to scattering in colloids.

Many results of the theory, in particular the reciprocity relation, were established by Krishnan before the advent of the theory, but a number of other consequences remain to be tested by experiments. One of these is the relation $\rho_v/\rho_h = \frac{1}{2} (1 - q/p)^2$ between the ratio of the depolarisation factors and the ratio of the photoelastic constants. Another is the variation of the intensities of the scattered light components with the direction of observation

$$V_v = A p^2$$

$$H_h = A (q \sin^2 \psi - p \cos^2 \psi)^2$$

$$H_v = V_h = B (q - p)^2 \sin^2 \psi$$

A and B are constant factors, p and q are the strain-optical constants and 2ψ is the angle between the directions of observation and of the incident light. We note that H_h vanishes for observations at a critical angle $2\psi_0$, where

$$\tan^2 \psi_0 = p/q$$

For this direction $\rho_h = V_h/H_h$ must have a sharp maximum. Since $2\psi_0$ will usually differ from 90° we conclude that the dependance of ρ_h on the angle of observation must be asymmetrical. For liquids with a positive constant of streaming birefringence and for most glasses ($p > q$) the maximum occurs for an angle larger than 90° . If the streaming birefringence is negative the angle $2\psi_0$ should be smaller than 90° . An experimental verification of this relationship will furnish a simple method for the determination of the ratio between the photoelastic constants.

In a recent paper Krishnan (1938 *a*) reports observations on a graphite sol which show an asymmetric ρ_h (2ψ) curve with a maximum markedly larger than 90° . This may be considered as a partial verification of the theory and may serve as a further indication for the applicability of the theory to the scattering of light in colloids.

In his latest paper, Krishnan (1938 *b*) has discovered a new property of structure scattering which appears to be of considerable significance. It was found that the depolarization factors ρ_h , ρ_v and ρ_u of the light scattered by a graphite sol undergo rapid changes if the colloid is made anisotropic by the application of a magnetic field. We will show here that this phenomenon can be explained on the basis of our theory.

To choose a simpler case which can be treated rigorously we consider the scattering of light in a glass block which has been made optically anisotropic by the application of a uniform elastic strain. The birefringence due to this strain is assumed to be large in comparison with the birefringence created by the random distribution of "frozen in" strains which are responsible for the scattering in glasses. Since the latter strains are very small the above assumption is compatible with a second assumption that the uniform birefringence is small, ϵ , with a difference of the refractive indices of the order of magnitude 10^{-4} . An experimental test will therefore require pressures of a magnitude commonly used in photoelastic investigations.

On the basis of the second assumption we can expect that Brillouin's law for the scattering by a single elastic wave is still valid and that the direction and frequency of the elastic "Bragg wave" is essentially the same as in the case of an isotropic solid¹. For plane polarised incident light of unit intensity, the light scattered by a unit volume to a point at the distance $R = 1$ has therefore the intensity

$$I = \frac{\pi^2}{\lambda_0^4 c} U(k_B) D_n^2(k_B),$$

where λ_0 is the wave-length of the light, and U the energy density of the Bragg wave. D_n is the component normal to the direction of observation of a vector D defined by the tensor equation $D = |\epsilon_{yz}| E_0$. E_0 is the electric vector of the incident light and the tensor $|\epsilon_{yz}|$ determines the amplitudes of the variations of the optical dielectric constant which a Bragg wave of amplitude $1/k_B = \lambda_0/4\pi n \cos \psi$ would create. For longitudinal waves, c has the value of the elastic constant c_{11} , for transversal waves $c = c_{44}$. So far, the mathematical formulation is identical with that for scattering in an isotropic

¹ This would not be true if the uniform birefringence were large.

glass The effect of the uniform strain becomes apparent when we turn to the calculation of the tensor ϵ_{yz}

In a previous paper on the diffraction of light by supersonic waves in crystals the author (Mueller, 1937) has pointed out that the photoelastic effects of a sound wave are essentially different for optically isotropic and anisotropic media In an isotropic solid the elastic strains change the index ellipsoid from a sphere into an ellipsoid, whereby the orientation of the axes of this ellipsoid is definitely fixed by the directions of propagation and vibration of the elastic wave In an optically anisotropic medium, however, the refractive properties are normally determined by an ellipsoid, and the effect of a sound wave consists mainly in producing fluctuations of the lengths of the principal axes To be sure the sound wave creates also small fluctuating changes of the direction of the axes, but these changes are small and can be neglected in the calculation of the optical diffraction effects, provided that the original birefringence is much larger than the photoelastic effects of the sound wave

A simple example may serve to illustrate the situation We consider the optical effects of a transversal elastic wave in a glass which is strained in the direction of propagation of the wave If this direction is denoted by x , and if y is the direction of vibration, the sound wave creates a fluctuating strain x_y The uniform constant strain is x_z The combined photoelastic effect of both strains is given by Pockels' equations

$$\left. \begin{aligned} a_{11} &= 1/n^2 + p_{11} x_x \\ a_{22} &= a_{33} = 1/n^2 + p_{12} x_x \\ a_{23} &= a_{31} = 0 \\ a_{13} &= p_{44} x_y = \frac{1}{2}(p_{11} - p_{12}) x_y \end{aligned} \right\} \quad (1)$$

where the polarisation constants a_{ik} determine the index ellipsoid

$$a_{11} x^2 + a_{22} y^2 + a_{33} z^2 + 2 a_{12} xy = 1 \quad (2)$$

One axis of this ellipsoid coincides with the z -axis, the two others are in direction X and Y which form an angle Θ with the x and y axes, respectively Θ is given by the relation

$$\tan 2 \Theta = 2 a_{12} / (a_{11} - a_{22}) = x_y / x_x \quad (3)$$

For an isotropic glass $x_x = 0$, hence $\Theta = 45^\circ$ and the principal axes a_x and a_y of the fluctuating index ellipsoid are everywhere at 45° to the direction of propagation In a strained glass, however, the angle Θ fluctuates with the period of the sound wave If the constant strain x_z is of the same order of magnitude as the amplitude of the variable strain x_y , the calculation of the diffraction effects must be very difficult A simple case is reached again when the constant strain is sufficiently large In this case Θ is very small

and the fluctuation of the direction of the axes can be neglected. Their orientation is fixed by the direction of the constant strain x_x

The lengths of the principal axes of the ellipsoid (2) are

$$\begin{aligned} a_x &= a_{11} \cos^2 \Theta + a_{22} \sin^2 \Theta + a_{12} \sin 2\Theta \\ a_y &= a_{11} \sin^2 \Theta + a_{22} \cos^2 \Theta - a_{12} \sin 2\Theta \\ a_z &= a_{33} \end{aligned} \quad (4)$$

For the strain-free material this reduces to

$$\begin{aligned} a_x &= 1/n^2 + p_{44}x_y \\ a_y &= 1/n^2 - p_{44}x_y \\ a_z &= 1/n^2 \end{aligned} \quad (5)$$

If the uniform strain is large $\sin \Theta$ and $\sin 2\Theta$ are negligible and hence

$$\begin{aligned} a_x &= a_{11} = 1/n^2 + p_{11}x_x \\ a_y &= a_{22} = 1/n^2 + p_{11}x_x \\ a_z &= a_{33} = 1/n^2 + p_{12}x_x \end{aligned} \quad (6)$$

The fluctuating terms in the equations (5) and (6), $\propto \epsilon$, those proportional to x_y , give rise to optical diffraction effects and to light scattering. Hence we see that in a strain-free glass the transversal waves produce optical effects but in a strained glass in which the strain is parallel to the direction of propagation the optical effects of the transversal wave must become very small, because in first approximation the equation of the optical index ellipsoid contains no fluctuating terms.

If the homogeneous strain has an arbitrary direction, the optical effects will not disappear but they will be different from what they are in the isotropic glass. This holds true also for longitudinal waves. Equations similar to (3) hold for every case, $\propto \epsilon$, the optical effect of a sound wave depends on the ratio between the variable and constant strain. If this ratio is small the diffraction effect differs very little from that in the isotropic glass. If this ratio is large a new type of diffraction or scattering effect must appear. After the new type has been reached a further increase of the uniform strain has no influence. The transition from one to the other type occurs when the uniform strain is of the same order of magnitude as that due to the sound wave. In the transition range the optical effects change rapidly with variations of the strain, but it is difficult to calculate the transition curves.

It should prove interesting to study experimentally the changes of the polarisation and intensity of the light diffracted by supersonic waves and of the intensity and depolarization factors of the scattered light in a glass or a cubic crystal while the solid is subjected to a slowly increasing pressure. The changes should set in quite suddenly when a critical pressure is reached and stop again above a certain pressure. From these critical pressures it will

be possible to estimate the amplitude of supersonic waves in solids and the magnitude of the fluctuations which are responsible for the scattering of light

It is clear that any other effect which produces birefringence, as for instance the Kerr effect, can be used to change the diffraction phenomenon. It is interesting to note that in cubic crystals, where the scattering is mainly due to temperature fluctuations, an extremely small artificial birefringence should change the depolarisation factors of the scattered light. It should therefore be possible to discover the Kerr effect in these crystals by means of scattering experiments, even if the birefringence is too small to be observed by any other method.

Krishnan's measurements of the changes of the depolarisation factors of the light scattered by a graphite sol under the influence of a magnetic field are in agreement with our conclusions. They change rapidly for the smallest applied fields (about 1,000 Gauss) and reach a stationary value for strong fields. Krishnan ascribes this saturation phenomenon to complete orientation of the graphite particles by the magnetic field. The preceding consideration furnishes another possible explanation. Saturation should occur also if the magnetic birefringence surpasses in magnitude the variations of the refractive index within the colloid. This might be reached before all particles are completely oriented.

Krishnan has investigated three cases of transverse scattering in a magnetic field. In case I the field is normal to the plane of observation, i.e., the plane parallel to the directions of observation and to that of the incident light. In case II the field points in the direction of observation and in case III it is parallel to the incident light. We will calculate here the analogous three cases of transverse scattering in a glass with a large uniform strain in either one of the above three directions.

For the isotropic glass the intensities of the scattered light components for transversal observation are

$$\begin{aligned} V_v &= \frac{\pi^2 n^8}{\lambda_0^4} \frac{U_L}{c_{11}} p_{11}^2 \\ H_h &= \frac{\pi^2 n^8}{\lambda_0^4} \frac{U_L}{c_{11}} p_{44}^2 \\ H_v = V_h &= \frac{\pi^2 n^8}{\lambda_0^4} \frac{U_T}{c_{44}} \frac{1}{2} p_{44}^2 \end{aligned} \quad (7)$$

To find the corresponding values for the strained glass we must calculate the tensor ϵ_{ij} for each one of the three Bragg waves (one longitudinal, L, and two transversal, l and T) and perform for each of the three cases the same type of calculation as was described in full detail for the isotropic glass (Mueller, 1938). The principal axes of the tensor ϵ_{ij} coincide with those of

the fluctuating index ellipsoid Referred to these axes the components ϵ_{yz} , ϵ_{zx} , ϵ_{xy} vanish and the diagonal terms are found by multiplying the fluctuating term in the expression for a_x , a_y and a_z (Equation 4) with n^4 The successive steps of the calculation are therefore as follows

1 Calculate the strains created by the three Bragg waves of amplitude $1/k_b$ The results are identical with those for an isotropic glass

2 With the help of Pockels' equation find the index ellipsoid Determine the direction of the principal axes by assuming that the constant strain is infinitely large Calculate the fluctuating term of a_x , a_y and a_z and multiply their value with n^4 This calculation has been illustrated in an example

3 Calculate D and D_n and the two components of D_n parallel and normal to the plane of observation for the two cases where the incident light vibrates either parallel or vertical to the plane of observation The intensities V_r , H_h , V_h and H_v are found by introducing the four values of the components of D_n into Brillouin's equation This procedure is analogous to that described for isotropic media

Since all calculations are quite elementary it is sufficient to present the results The tables below give the values of ϵ_{xx}/n^4 , ϵ_{yy}/n^4 , ϵ_{zz}/n^4 and the directions of the axes of the tensor These directions are given by the letters in brackets They have the following meaning

- (*h*) direction of the incident light
- (*i*) direction of observation
- (*v*) perpendicular to plane of observation
- (*b*) direction of propagation of Bragg wave at 45° to (*h*) and (*i*)
- (*t*) normal to (*b*) in the plane of observation
- (*u*) and (*v*) are bisecting the angles between (*h*) and (*i*)
- (*m*) and (*n*) are bisecting the angles between (*i*) and (*v*)

These letters are used also to give the directions of the strains and the direction of vibration of the elastic waves

Case I Strain (*v*)

L-wave (<i>b</i>)	<i>t</i> -wave (<i>t</i>)	T-wave (<i>v</i>)
p_{11} (<i>b</i>)	p_{44} (<i>i</i>)	0 (<i>h</i>)
p_{12} (<i>i</i>)	$-p_{44}$ (<i>h</i>)	0 (<i>t</i>)
p_{12} (<i>v</i>)	0 (<i>v</i>)	0 (<i>v</i>)

Case II Strain (*i*)

$\frac{1}{2}(p_{11} + p_{12})$ (<i>i</i>)	p_{44} (<i>i</i>)	0 (<i>i</i>)
$\frac{1}{2}(p_{11} + p_{12})$ (<i>h</i>)	$-p_{44}$ (<i>h</i>)	$p_{44}/\sqrt{2}$ (<i>u</i>)
p_{12} (<i>v</i>)	0 (<i>v</i>)	$-p_{44}/\sqrt{2}$ (<i>v</i>)

Case III Strain (*h*)

L-wave (<i>b</i>)	<i>t</i> -wave (<i>t</i>)	T-wave (<i>v</i>)
$\frac{1}{2} (p_{11} + p_{12}) (t)$	$p_{44} (t)$	0 (<i>h</i>)
$\frac{1}{2} (p_{11} + p_{12}) (h)$	$- p_{44} (h)$	$p_{44}/\sqrt{2} (m)$
$p_{12} (v)$	0 (<i>v</i>)	$- p_{44}/\sqrt{2} (n)$

For the transversal wave *t* the ϵ_{yz} tensor is in all cases the same as for the unstrained solid. Since this wave produces no scattering in the isotropic glass it remains inactive also in the strained glass.

In case I the L-wave gives the same tensor as in the isotropic glass. Hence V_v and H_h are given by equation (7). The transversal T-wave is inactive, hence $H_t = V_h = 0$. The reciprocity relation is valid.

In the cases II and III the L-wave produces only a component V_v . It has the same value as for the isotropic glass. In case II the T-wave gives rise only to a component H_v of the same magnitude as in the isotropic glass. Since V_h vanishes, the reciprocity relation does not hold. The same is true for case III because H_v vanishes and only V_h exists with the same magnitude as given in equation (7).

In the chart below the predictions of the theory for a strained glass are compared with Krishnan's observations for a graphite sol in a magnetic field. The numbers are the ratios between the original values of the depolarisation factors for zero field and their saturation values for large fields.

	Case I		Case II		Case III	
	theor	obs	theor	obs	theor	obs
V_v	no change	increase	no change	decrease	no change	decrease
H_h	no change	increase	decrease	decrease	decrease	no change
V_h	decrease	no change	decrease	no change	no change	increase
H_v	decrease	no change	no change	increase	decrease	decrease
ρ_h	decrease	decr (7)	0/0	incr ($\frac{1}{2}$)	increase	incr (1/12)
ρ_v	decrease	decr (3)	no change	incr ($\frac{1}{2}$)	decrease	decr (1/2)
R R	valid	valid	not valid	not valid	not valid	not valid

Complete agreement exists only concerning the validity of the reciprocity relation (R R). The intensities do not change in accordance with the theory. The cause for this discrepancy is to be found in the fact that for the glass we have assumed that the random distribution of Bragg waves

is not disturbed by a strain. For a colloid with oriented anisotropic particles this assumption is not tenable. If the optical fluctuations in an anisotropic colloid are represented by a Fourier series the number of plane waves in a small angular range and their amplitudes will depend on the direction of the wave vector and will vary with the strength of the magnetic field. A more complete theory for colloids should take into account that U_L and U_T in equation (7) depend on the magnetic field. The disagreement between the calculated and observed change of the intensities is therefore not surprising. Variations of U_L and U_T change also the depolarisation factors, but this change is most probably smaller than that of the intensities because the depolarisation factors are proportional to the ratio U_T/U_L . We believe therefore that it is significant that the theory gives the correct changes of ρ_h and ρ_v for the cases I and III. For case II, the theory gives for ρ_h the undetermined value 0/0, hence a definite disagreement exists only for one out of the six values for the depolarisation factors.

The large influence of a small forced birefringence on the intensities and depolarisation factors is a characteristic property of "Brillouin scattering", i.e., of scattering in a medium in which the optical fluctuations in neighbouring volume elements are not independent. Since this effect does not exist for "Raleigh scattering" in gases and ordinary liquids it will furnish a crucial test for distinguishing the two types of light scattering phenomena.

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Summary

The theory of Brillouin scattering of light in an optically anisotropic medium is developed. The influence of a uniform elastic strain on the intensity and the depolarisation factors of the light scattered by a glass are calculated. These quantities change rapidly when the forced birefringence reaches a magnitude of the same order as the optical fluctuations within the glass. They reach definite saturation values for large strains. The results are analogous in many respects to those observed for scattering in a graphite sol under the influence of a magnetic field.

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UNTERSUCHUNG VON SCHALLAMPLITUDEN- FELDERN MITTELS EINER METHODE DER ISOCHROMATEN.

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ZUSAMMENFASSUNG Die Sichtbarmachung der Schallamplitudenfelder erlaubt eine besonders genaue Untersuchung der Abstrahlung von Schallquellen. Es wird u. a. eine Schall-Interferenz-Erscheinung im Gebiet weniger Wellenlängen vor der Quelle festgestellt, die bisher theoretisch noch nicht behandelt wurde. Bei Durchstrahlung des Schallfeldes mit weissem Licht erhält man farbige Bilder des Amplitudenfeldes, die einem grossen Auditorium vorgeführt werden können. Die Linien gleicher Amplitude erscheinen als Linien gleicher Farbe, als Isochromaten. Einige Farbenphotographien zeigen die Verwendbarkeit der Methode zur Beurteilung der Energieverteilung im Schallfeld.

In einem stationären Schallfeld in einer homogenen Flüssigkeit ist die Schwankung der Dichte und der Brechungsindex an einer bestimmten Stelle nur eine Funktion der Schallamplitude. Man kann daher die Verteilung der Schallamplitude z. B. mittels der Toepler'schen Schlierenanordnung sichtbar machen. Man bildet nämlich eine Lichtquelle durch das zu untersuchende Medium hindurch ab und verdeckt gerade das Bild der Lichtquelle, es wird dann von der Blende nur solches Licht vorbeigelassen, dass an Inhomogenitäten im Schallfeld gebeugt wird. Inhomogenitäten sind in einem Schallfeld durch die Dichte- und Brechungsindex-schwankungen verursacht. Je grösser die mittlere Dichteschwankung an der betreffenden Stelle des Schallfeldes ist, um so mehr Licht wird im zeitlichen Mittel von dieser Stelle abgelenkt. Bildet man das Schallfeld mit alleiniger Benutzung des abgelenkten Lichtes ab, so erhält man eine einfache Abbildung der Amplitudenverteilung im Schallfeld, die schon auf Aufnahmen von Tawil¹ zu erkennen ist.

Die Sichtbarmachung des Schallamplitudenfeldes mittels der Toepler'schen Methode wird experimentell besonders einfach bei hohen Ultraschallfrequenzen, bei denen die Schallwellen als optisches Beugungsgitter wirken. Man kann dann, wie R. Bár,² sowie E. Hiedemann und K. H. Hoesch³ (vgl. auch S. Parthasarathy⁴) nahezu gleichzeitig gezeigt haben, an dem Ort der vom Schallwellengitter erzeugten Beugungsspektren eine Blende anbringen

und z B nur eine einzige Ordnung zur Sichtbarmachung des Schallfeldes benutzen. Verwendet man als Lichtquelle einen Spalt, so kann man zur Ausblendung ebenfalls einen Spalt benutzen, wie die Fig 1 zeigt. Diese Anordnung ist so lichtstark, dass man sie zur Demonstration von Schallamplitudenfeldern vor einem grossen Auditorium anwenden kann.⁵ Die Lichtquelle

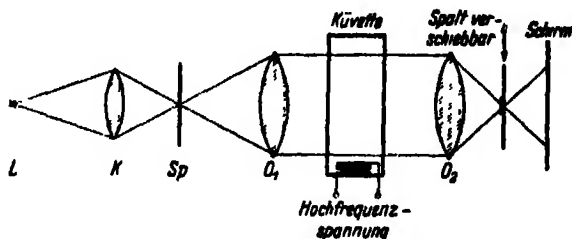


FIG 1

L , wird durch einen Kondensor K auf einen Spalt konzentriert, der im Brennpunkt des Objektivs O_1 steht, so dass aus diesem paralleles Licht in die Kuvette eintritt, in welcher ein Piezoquarz Ultraschallwellen senkrecht zur Lichtrichtung aussendet. Mittels des Objektivs O_2 wird ein Spaltbild an einer Stelle entworfen, an der ein horizontal verschiebbarer Spalt angebracht ist. Für genauere Untersuchungen muss man natürlich eine beleuchtete Lochblende als Lichtquelle und eine zweite Lochblende für die Beobachtung in der nullten Ordnung oder Ringblenden für die höheren Ordnungen benutzen. Die Methodik der Sichtbarmachung des Schallamplitudenfeldes wurde bisher besonders von E. Heidemann und Mitarbeitern ausgebaut. Die Verfasser haben die Methode u a auch für systematische Untersuchungen des Schallfeldes vor Quarzen angewendet.⁶

Bei der optischen Untersuchung der Schallabstrahlung einer Schallquelle muss man beachten, dass ein durch ein Ultraschallfeld fortschreitender Lichtstrahl an allen Stellen seines Weges durch das Schallfeld von diesem beeinflusst wird. Die Einwirkung des Schallfeldes auf den Lichtstrahl ist von der Intensität und der Richtung der Schallwellen abhängig. Aus den optischen Erscheinungen können daher nur dann genauere Aussagen über das Schallfeld erhalten werden, wenn ebene Schnitte durch das Schallfeld senkrecht zur Lichtrichtung einander gleich sind. Experimentell lässt sich diese Bedingung mit grosser Annäherung verwirklichen, wenn man Ultraschallquellen verwendet, deren Länge in der Lichtrichtung sehr gross gegenüber ihrer Breite ist. Ferner muss die Amplitude der Schallquelle parallel der Lichtrichtung möglichst konstant sein. Diese Bedingungen können entweder durch Benutzung von langen Spalten erfüllt werden, auf die ebene

homogene Schallwellen auftreffen, oder durch Quarzstäbe besonderer Form In Fig 2 ist der von E Hiedemann angegebene Schnitt dieser Stäbe ange-

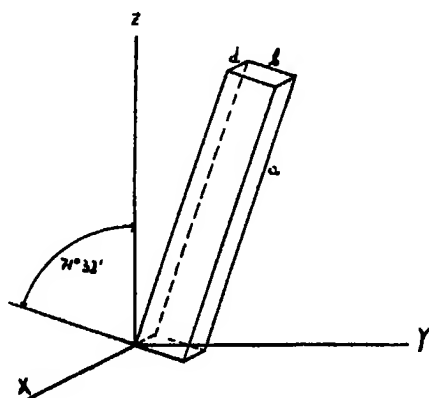


FIG 2

deutet Um möglichst kolbenförmige Schwingung der Stirnflächen zu erhalten, wurde entsprechend den Ergebnissen von H Straubel⁷ sogenannte 71°—Stäbe gewählt, jedoch wurden diese Stäbe so geschnitten, dass ihre grösste Länge senkrecht zur 71° 32'—Richtung ist, während sonst bei den 71°—Stäben die grösste Länge mit dieser Richtung übereinstimmt Die grösste Länge des Stabes sei mit a bezeichnet, die Dicke in der x -Richtung (der elektrischen Achse) mit d und die andere Kantenlänge mit b Die z -Achse der Zeichnung ist gemäss der üblichen Bezeichnungsweise die optische Achse des Quarzes und die y -Achse ist die zu ihr und der elektrischen Achse senkrechte Achse Die Elektroden werden auf den Flächen senkrecht zur x -Achse, also auf die a - b -Flächen angebracht und die Abstrahlung des Quarzes von einer a - d -Stirnfläche wird beobachtet Solche Quarzstäbe sowie geeignete Spalte erlauben einen Vergleich mit den theoretischen Berechnungen des Schallfeldes vor Schallquellen bei denen praktisch immer eine kolbenförmige Schwingung des Schallgebers angenommen wird Der Fall ist natürlich analog dem optischen Beispiel der Beugung von parallelem Licht an einer Blende

Die bisherigen Untersuchungen über die Schallabstrahlung zeigen eine sehr befriedigende Uebereinstimmung mit der Theorie.⁸ Die Tafel I zeigt die Schallamplitudenfelder vor Quarzstäben verschiedener Dicke D Man erkennt deutlich die Richtungen maximaler und minimaler Schallabstrahlung Der Öffnungswinkel des Hauptstrahles nimmt mit wachsendem Wert von D/λ ab, wie ja theoretisch zu erwarten ist Aus den Aufnahmen ist ferner ersichtlich, dass der Hauptstrahl bei niedrigeren Werten von D/λ praktisch unmittelbar vor der Schallquelle ansetzt, während er sich bei höheren Werten

von D/λ erst in einiger Entfernung ausgebildet, und zwar in umso grosserer Entfernung, je grosser D/λ ist. Gleichzeitig tritt bei hohen Werten von D/λ ein bisher von der Theorie unseres Wissens noch nicht berechnetes Interferenzmuster auf, das in der letzten Aufnahme der Tafel vergrössert wiedergegeben ist. Das Interferenzmuster entsteht auch hinter Spalten, auf die eine ebene Schallwelle trifft, ist also nicht etwa verursacht durch eine Chaldni-Figur des Quarzes. (Eine Andeutung dieses Interferenzmusters ist übrigens schon auf einer früheren Aufnahme von R. Bar⁹ zu erkennen.) Das Aussehen der Interferenzerscheinung und die Zahl der auftretenden Maxima ist lediglich eine Funktion von D/λ . (Die Zahl der Interferenzmaxima wächst mit wachsendem Wert von D/λ .)

Diese Bilder zeigen, dass sehr grosse Feinheiten des Schallfeldes sichtbar gemacht werden können, z. T. auch solche, die mit keinem anderen Beobachtungsverfahren erkannt werden können. Gemäss den grundlegenden Beobachtungen von Debye und Sears,¹⁰ sowie von Lucas und Biquard¹¹ ist die Intensität des abgelenkten Lichtes—abhängig von der Schallintensität. Der genaue quantitative Zusammenhang zwischen der Intensitätsverteilung über die Beugungsordnungen ist bekanntlich durch die Theorie von Raman und Nath¹² gegeben. Auf Grund dieser Zusammenhänge entsprechen die Linien gleicher Schwärzung den Kurven gleicher Schalldruck-Amplitude. Bei Benutzung von weissem Licht, wie bei den Aufnahmen der Tafel I erkennt man zwar die Linien gleicher Amplitude, aber man erhält doch kein eindeutiges Bild der Energieverteilung, man kann z. B. nicht übersehen, dass mehr als 90 % der Schallenergie in dem Hauptstrahl enthalten ist.

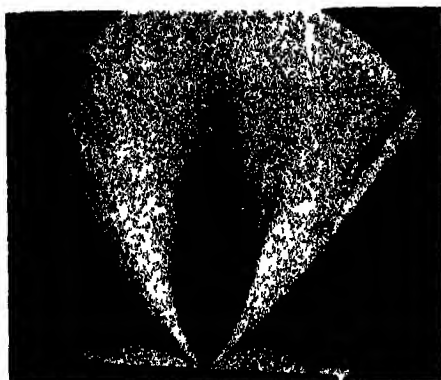
Diesen Nachteil kann man durch Benutzung von monochromatischem Licht beheben, es lässt sich dann aus der Schwärzung der Platte gemäss den von Raman und Nath angegebenen Beziehungen sogar quantitativ die Amplitudenverteilung im Schallfeld studieren und ebenfalls die Schallabsorption bestimmen. Über solche noch nicht abgeschlossenen Versuche wird später an anderer Stelle berichtet werden. Zur Vermiedung von Wärme—Schlieren im Schallfeld muss man kurze Belichtungszeiten benutzen. Monochromatische Lichtquellen, deren Lichtstärke so gross ist, dass sie die Aufnahme von Schlierenbildern mit kurzen Belichtungszeiten gestatten, stehen aber nicht immer zur Verfügung. In vielen Fällen—besonders für Demonstrationen—wird man daher die Verwendung von weissem Licht vorziehen. Bei der visuellen Beobachtung und Demonstration mit weissem Licht erhält man aber ein recht gutes Bild der Energieverteilung infolge der auftretenden Farben-Effekte. Die Menge des abgelenkten Lichtes ist ja nicht nur eine Funktion der Schallamplitude und des Lichtweges im Schallfeld, sondern auch der Lichtwellenlänge. Man erhält daher bei Verwendung

von weissem Licht ein farbiges Bild des Schallfeldes. Entwirft man das Bild des Amplitudenfeldes mit der nullten Beugungsordnung, so beobachtet man Komplementärfarben, die durch Lichtbeugung in die höheren Ordnungen entstehen. Beobachtet man mit einer höheren Ordnung, so erhält man Bilder, deren Farben unmittelbar anzeigen, welche Wellenlängen am stärksten abgelenkt werden. Linien gleicher Amplitude werden als Linien gleicher Farbe, als Isochromaten sichtbar. In der in Fig. 1 skizzierten Anordnung kann man die verschiedenen farbigen Bilder besonders einfach demonstrieren, wenn man die verschiebbare Spaltblende von der nullten in andere Ordnungen verschiebt. Als die Verfasser im vorigen Jahre die Gelegenheit hatten, diese Versuche Sir Raman zu demonstrieren, riet dieser zur Aufnahme von Farbenphotographien. Die Verfasser haben dieser Anregung gerne entsprochen und zeigen hier einige Beispiele in der Farbentafel. Die Aufnahmen sind absichtlich in der nicht ganz genauen—aber für Demonstrationen besonders geeigneten—Spalt-Anordnung ausgeführt und es sind lediglich Bilder der nullten Ordnung benutzt. Die erste Aufnahme der Farbentafel zeigt das Schallfeld vor einer grosseren Quarzplatte (einem normalen x-Schnitt). Man erkennt deutlich die schiefe Abstrahlung des Quarzes. Die folgenden Aufnahmen sind mit nahezu kolbenförmig schwingenden Quarzstäben des beschriebenen Schnittes ausgeführt. Für die zweite Aufnahme war ein verhältnismässig kleiner Wert von D/λ gewählt, für die beiden letzten ein grosserer. Man kann auf allen drei Bildern geschlossene Isochromaten sehen. Die Ausdehnung der von gleichfarbigen Kurven umschlossenen Flächen gibt ein Bild der Energieverteilung im Schallfeld. Die geschlossenen Kurven entsprechen sehr befriedigend den theoretisch berechneten Kurven. Eine genaue quantitative Uebereinstimmung mit den theoretischen Kurven kann deshalb nicht erwartet werden, weil bei diesen die Schallabsorption vernachlässigt wird. Dass das von einer Isochromate umschlossene Gebiet bei starker Schallabsorption kleiner wird, lässt sich sehr schon durch einen Vergleich der beiden letzten Aufnahmen zeigen, die mit wenig verschiedenen Werten von D/λ ausgeführt sind, aber in Flüssigkeiten sehr verschiedener Schallabsorption. Bekanntlich ist die Ultraschallabsorption in Benzol sehr viel grösser als in Xylol. Auf die Auswertung dieser Farbaufnahmen zur Untersuchung der Richtcharakteristik von Schallquellen und zum Vergleich der Schallabsorption in Flüssigkeiten soll an dieser Stelle nicht näher eingegangen werden, da hier nur das Prinzip der Methode erklärt werden sollte.

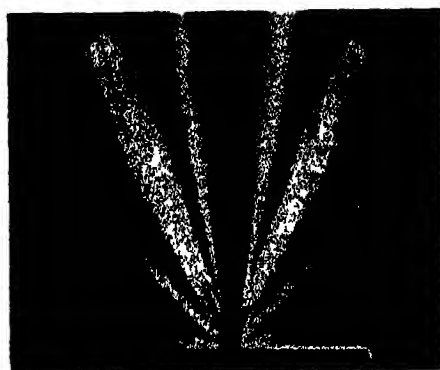
Wir mochten auch an dieser Stelle Herrn Prof. Raman herzlich für die Anregung zur Ausführung der Farbenphotographien danken, sowie der Indischen Academie der Wissenschaften für die Ermöglichung der Reproduktion dieser Aufnahmen.

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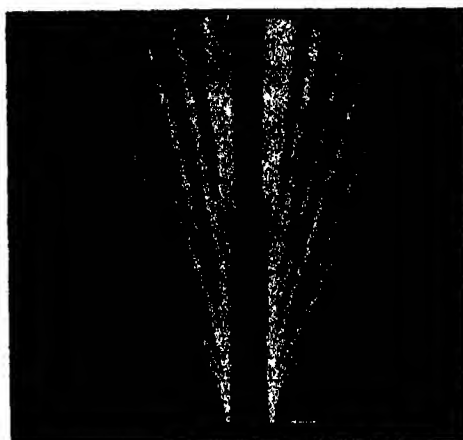
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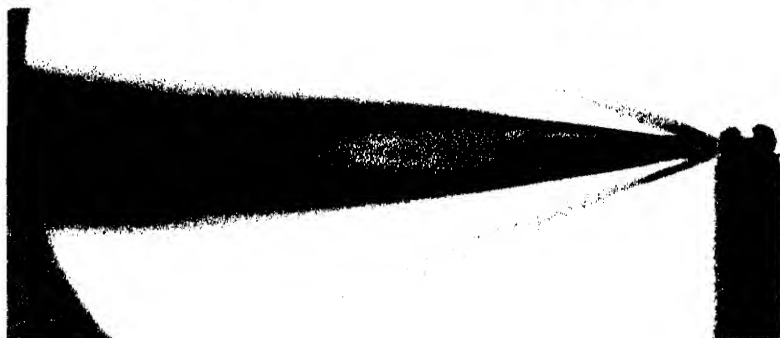
D-142A

Xylene

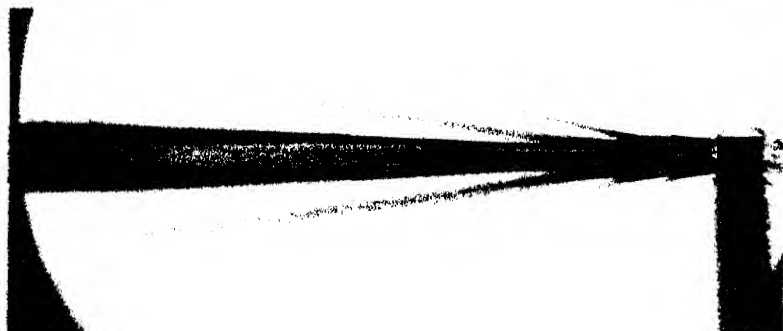
D = A
 $\text{C}_6\text{H}_4(\text{CH}_3)_2$



D = 4,7 A
 $\text{C}_6\text{H}_4(\text{CH}_3)_2$



D = 10,8 A
 $\text{C}_6\text{H}_4(\text{CH}_3)_2$



D = 11 A
 C_6H_6



UBER BIOLOGISCHE WIRKUNGEN ULTRAVIOLETER LICHTQUANTEN.

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IN diesem Jubiläumsbande, in welchem Physiker aller Länder Venkata Raman ihre Glückwünsche ausdrücken, mag es erlaubt sein, auch einen solchen Gegenstand zu berühren, der nicht mehr der reinen Physik, sondern dem physikalisch-biologischen Grenzgebiet angehört. Es handelt sich um ein Untersuchungsgebiet, das für die Biologie von großer grundsätzlicher Bedeutung ist, und welches dem Physiker Gelegenheit gibt, die Kenntnisse anzuwenden, welche wir durch die Quantentheorie der Lichtwirkungen gewonnen haben, und zu deren Entwicklung die Forschungen Venkata Ramans so wesentliche Beiträge geliefert haben.

Wir beschäftigen uns im folgenden insbesondere mit *Bacterium coli*—kleinen, ungefähr zylindrischen Zellen von 2μ Länge und $0,5\mu$ Durchmesser. In mannigfaltigen Experimenten verschiedener Verfasser ist die *Totung* derartiger Zellen durch verschiedene Einwirkungen untersucht. Insbesondere durch ultraviolette Bestrahlung, aber auch durch Röntgen- und γ -Strahlen, Kathoden- und β -Strahlen, α -Strahlen, und auch durch mancherlei Gifte, wie z. B. Phenol oder HgCl_2 .

Dabei zeigt es sich, daß die gleichformige Einwirkung des betreffenden Totungsmittels auf eine Anzahl möglichst homogen gewählter Zellen keineswegs zu einem Absterben aller dieser Zellen im gleichen Zeitpunkt führt. Vielmehr erweist sich die Abtötung als ein *unstetiger Vorgang*, dessen Eintreten—analog atomphysikalischen Elementarprozessen—einem bestimmten *statistischen* Gesetz unterliegt. Und zwar ist dies Gesetz (von einer einzigen noch zu besprechenden Ausnahme abgesehen) in allen erwähnten Fällen das einfachste überhaupt denkbare. *Die Anzahl der überlebenden Zellen klingt bei konstanter Einwirkung des todenden Agens exponentiell ab.*

Über die Bedeutung dieses Ergebnisses kann offenbar kein Zweifel bestehen. Wir sehen, daß z. B. im Falle des ultra-violetten Lichtes die Totung das Ergebnis *einer einzigen* $h\nu$ -Absorption ist. Oder, daß bei der Vergiftung mit Phenol oder HgCl_2 *ein einziger* Molekularprozeß zur Totung führt. Dabei werden allerdings im Mittel sehr viele Lichtquanten ($\approx 10^6$) absorbiert, bevor die Totung erfolgt, und es dringen sehr viele Moleküle des Giftes in die Zelle ein. Aber sowohl ein in der Zelle absorbiertes $h\nu$ als auch

ein in die Zelle eingedrungenes Giftmolekül bleiben in den meisten Fällen völlig unschädlich, nur als seltener Ausnahmefall ergibt sich ein quantenphysikalischer Elementarprozeß, der nun sogleich nicht etwa nur zu einer geringfügigen Schädigung, sondern zur vollständigen Totung der Zelle führt

Die Zelle verhält sich also in gewissem Sinne so, als wenn sie selber nur ein einziges großes Molekül wäre. Aber natürlich ist das nicht der Fall. Die richtige Auffassung der Sachlage ist vielmehr die, daß wir uns in der (vom atomphysikalischen Standpunkt aus *riesig großen*) Zelle ein einzelnes Molekül oder eine kleine Gruppe von Molekülen vorstellen, welche eine singuläre Ausnahmestellung innerhalb der Zelle besitzen. Man kann diese Gruppe von Molekülen anschaulich als das *Steuerungszentrum* der Zelle bezeichnen. Offenbar handelt es sich darum, daß diese Moleküle—wahrscheinlich durch katalytische Wirkungen—die Lebensfunktionen der Zelle weitgehend steuern, derart, daß ein das Steuerungszentrum außer Funktion setzender mikrophysikalischer Elementarprozeß (z. B. eine darin durch $h\nu$ -Absorption veranlaßte oder durch Reaktion mit einem einzelnen Giftmolekül bewirkte Umlagerung) die Lebensfähigkeit der Zelle zerstört.

Dass der Teil des Zellkörpers, in welchem ein einzelner Elementarprozeß todlich wirken kann, tatsächlich räumlich sehr klein ist, kann natürlich aus den Experimenten mit Ultraviolett oder mit Giften *nicht* herausgelesen werden.¹ Es wird aber bewiesen durch Erfahrungen mit monochromatischen Röntgenstrahlen verschiedener Wellenlängen. Die einfachste Vorstellung, die man sich von dem Verlauf der Totung durch Röntgenstrahlen (oder auch durch γ - und β -Strahlen) machen kann, ist offenbar diese: Ein das Zellplasma durchquerendes schnelles Elektron bringt längs seiner Bahn zahlreiche weitere Ionisierungen (und Anregungen) zustande. Nehmen wir an, daß *eine einzelne* dieser Ionisierungen todlich wirken kann, so werden wir, falls diese einzelnen Ionisierungen hinreichend weit auseinanderliegen, bei bestimmter Strahlendosis eine Wahrscheinlichkeit der Totung erhalten, die direkt proportional ist mit der räumlichen Dichte der erzeugten einzelnen Ionisierungen. Wenn nun eine einzelne Ionisierung an *jedem* Orte innerhalb der Zelle todlich wirken konnte, derart, daß die (dann entsprechend geringe) Wahrscheinlichkeit einer todlichen Auswirkung dieser Ionisierung praktisch konstant innerhalb großer Teilgebiete der Zelle wäre, so würde die oben abgeleitete Proportionalität der Totungswahrscheinlichkeit mit der Strahlendosis für beliebige Energien der das Zellplasma durchquerenden schnellen Elektronen gelten. Tatsächlich aber zeigt sich, daß die Totungswahrschein-

¹ Diese würden im Gegenteil auch eine über den Zellkörper gleichmäßig verteilte geringe Strahlen- oder Gift-Empfindlichkeit zulassen.

lichkeit pro Dosis-Einheit *abnimmt*, wenn wir zu sehr *weichen* Rontgenstrahlen übergehen sie ist bei 3 KV etwa halb so groß wie bei 22 KV Diese Abnahme wird verständlich, wenn wir uns die räumliche Verteilung der Strahlenempfindlichkeit jetzt so vorstellen, daß wir sagen Es gibt ein kleines Volumstück v_0 in der Zelle von solcher Art, daß jede in v_0 geschehende Ionisierung todlich wirkt, jede außerhalb von v_0 geschehende dagegen unschadlich bleibt Wenn wir nämlich jetzt mit sehr weichen Rontgenstrahlen arbeiten, sodaß die dadurch ausgelosten Elektronen langs ihrer Bahn eine *sehr dichte* Folge von Ionisierungen ergeben, so wird im statistischen Durchschnitt jedes Volumstück v_0 einer Zelle *entweder* keine *oder* gleich mehr als eine Ionisierung empfangen, offensichtlich ergibt das eine Verkleinerung der Totungswahrscheinlichkeit im Verhältnis zur Gesamtzahl der im cm^3 eingetretenen Ionisierungen

In der Tat werden wir also dazu genotigt, die Empfindlichkeit der Zelle gegenüber mikrophysikalischen Elementarakten als in einem sehr kleinen Bezirk lokalisiert anzunehmen. das Volum v_0 entspricht dem "Steuerungszentrum" der Zelle Die quantitative Durchführung der angedeuteten Betrachtungen ergibt Möglichkeiten, über die geometrischen Verhältnisse des Volums v_0 (wie etwa Zerteilung von v_0 in mehrere etwas getrennte Teilstücke) nähere Aufschlüsse zu erhalten

Offenbar ist die Größe von v_0 unmittelbar zu entnehmen aus der Totungswahrscheinlichkeit bei Anwendung von *harten* Rontgenstrahlen (oder γ - oder β -Strahlen); Definiert man nun in formal analoger Weise ein entsprechendes Volumstück für jede der untersuchten Wellenlängen des Ultravioletts, so findet man 10^2 bis 10^3 mal kleinere Volumina Dies ist ein sehr auffälliger Punkt, auf den wir zurückkommen wollen

Ferner ist bemerkenswert ein gewisser Ausnahmefall vom exponentiellen Verlauf der Totung Ultraviolett wurde monochromatisch angewandt (Wyckoff), und im Gegensatz zu mehreren anderen etwas kürzeren Wellenlängen ergab die Anwendung von 3132 \AA einen Totungsverlauf, der auf eine gewisse *Akkumulierung* in der Wirkung der absorbierten Lichtquanten hinweist

Ein anderer auffälliger Effekt zeigte sich bei der Tötung von *Hefe*, durch Strahlungen In diesem Falle läßt die Tötung durch Rontgenstrahlen wesentlich kompliziertere Verhältnisse erkennen, als bei *Bacterium coli* Wiederum beruht die Totung auf quantenphysikalischen Elementarprozessen, die im "Steuerungszentrum" der Hefezelle (das zweifellos mit dem *Zellkern* zu identifizieren ist) angreifen Jedoch handelt es sich um Elementarprozesse von etwas komplizierterer Art eine einzelne Ionisierung genügt nicht

oder hat zum mindesten nur relativ *geringe Wahrscheinlichkeit*, die fragliche molekulare (oder mizellare) Umlagerung hervorzurufen, treten aber an dem empfindlichen Orte *mehrere* (vielleicht nur 2 oder 3, vielleicht auch noch etwas mehr) Ionisierungen in enger räumlicher Nachbarschaft ein, so kann diese molekulare Umlagerung relativ leicht bewirkt werden

Die Tötung der Hefe durch ultraviolettes Licht ergibt nun etwas Merkwürdiges. Während der größte Teil des ultravioletten Spektrums anscheinend nicht instande ist, die fragliche durch Zusammentreffen mehrerer Ionisierungen erzwingbare Umlagerung hervorzurufen, weiß man (Schreiber), daß die Wellenlänge 2540 Å dazu befähigt ist. Ein einziges $h\nu$ dieser Wellenlänge vermag also dasselbe zu leisten, was bei Anwendung von Röntgenstrahlen *nicht* (oder nur selten) durch eine einzelne Ionisierung, sondern durch das Zusammenwirken mehrerer erzielt wird.

Die aufgezählten Punkte zeigen, daß die Ultraviolett-Experimente uns eine Reihe interessanter Eigenschaften der das Steuerungszentrum der fraglichen Zellen zusammensetzenden Moleküle erkennen lassen. Wie schon kurz erwähnt wurde, dürfen wir überzeugt sein, daß das Steuerungszentrum in den fraglichen Fällen mit dem *Zellkern* zu identifizieren (bzw. bei *Bacterium coli* als ein sehr kleiner, dem gewöhnlichen Mikroskop nicht mehr erfaßbarer Zellkern zu deuten) ist. Die besprochenen Experimente liefern uns also Aufschluß über die physikalischen Strukturverhältnisse der im Zellkern enthaltenen Moleküle. Man weiß, daß die Chromosomen eines Zellkerns einerseits aus einem Nukleinsäure-Gerüst und andererseits aus gewissen Eiweißmolekülen bestehen nämlich den "Genen", welche als die materiellen Träger der durch die Vererbungsforschung analysierten *Erbfaktoren* aufzufassen sind. Ueber diese Moleküle, die gewissermaßen die eigentlichen Zentren des Lebens sind, werden wir aus der Untersuchung ihrer Strahlungsreaktionen sehr viel lernen können, ähnlich, wie wir auch über die Strukturverhältnisse wesentlich kleinerer Moleküle durch ihre Lichtreaktionen, insbesondere aufgrund des *Ramaneffekts*, weitgehenden Aufschluß erhalten. Ein zu einer molekularen Umlagerung führender Quantensprung eines Genmoleküls ist, biologisch gesprochen, eine *Mutation*. Die besprochene Tötung von *Bact. coli* können wir als eine strahleninduzierte *letale Mutation* bezeichnen. Aber es gibt bekanntlich, und zwar nicht nur bei höheren Organismen, sondern auch z. B. bei Hefe (*Nadson*), auch vielerlei Mutationen von *nicht* letaler Wirkung.

Das experimentelle Material ist gegenwärtig noch viel zu wenig umfangreich, um uns eine mehr ins Einzelne gehende Strukturbestimmung der fraglichen Moleküle zu ermöglichen. Wenn wir trotzdem versuchen, einige

Bemerkungen zu den oben hervorgehobenen Punkten zu machen, so sind damit nicht so sehr endgültige Feststellungen beabsichtigt, als vielmehr ein Versuch, für weitere Arbeiten heuristische Anhaltspunkte zu geben

Für ein genaueres Verständnis der physikalischen Reaktionen der uns interessierenden organischen Riesenmoleküle scheint eine von Moglich und Schon ausgesprochene Idee besonders wertvoll. Nach diesen Verfassern ist anzunehmen, daß die inneren Strukturverhältnisse in derartigen Riesenmolekülen denjenigen ähnlich sind, welche wir von den *festen Körpern* kennen, in dem Sinne nämlich, daß die locker gebundenen Elektronen eines derartigen Moleküls nicht etwa stark lokalisiert sind (bei bestimmten Atomen oder in bestimmten Valenz-Strichen), sondern daß vielmehr in erster Approximation die Vorstellung berechtigt ist, daß die Elektronen gewisse in "Energiebändern" zusammen liegende Quantenniveaus besetzen, deren jedes dem *ganzen Molekül*, ohne Lokalisierung, angehört. Es soll also hier dieselbe Vorstellung angewandt werden, welche der Quantentheorie der metallischen Leiter, der Halbleiter und der Leuchtphosphore zugrunde liegt. Zugunsten dieser Vorstellung lassen sich verschiedene Tatsachen anführen, z. B. die von kleineren Molekülen her gut bekannte freie Beweglichkeit der Bindungselektronen im Benzolring und verwandten Verbindungen. Ferner wird diese Vorstellung begünstigt durch die Tatsache, daß viele der hochpolymeren organischen Substanzen lange Kettenmoleküle besitzen, in denen sich dasselbe Radikal vielfach wiederholt, sodaß ein mehr oder weniger *periodisches* Kraftfeld im Molekül besteht.

Die Brauchbarkeit der Hypothese von Moglich und Schon wird ferner illustriert durch die Eigenschaften eines gewissen Fermentes, der *Urease*. Man kennt von diesem Ferment einerseits das ultraviolette *Absorptionsspektrum*, und andererseits für mehrere verschiedene Wellenlängen das *Inaktivierungsspektrum* (Kubowitz-Haas)—das Ferment wird nämlich durch Ultraviolett-Bestrahlung inaktiviert. Obwohl in dem untersuchten Gebiete die Absorptionsstärke um einen Faktor der Größenordnung 5000 variiert, zeigt sich eine fast vollkommene *Proportionalität* der beiden Spektren, nur bei einer der untersuchten Wellenlängen (2540 Å) ist die relative Stärke der Inaktivierung verdoppelt.

Die Proportionalität beider Spektren ist aber sehr auffällig, weil der Proportionalitätsfaktor sehr stark von 1 verschieden ist. M. Delbrück, dem ich den Hinweis auf die interessanten Eigenschaften der Urease verdanke, hat bemerkt, daß der früher unbekannte Wert dieses Proportionalitätsfaktors jetzt bestimmt werden kann, nachdem inzwischen durch Sumner das Molekulargewicht der Urease bestimmt worden ist (es ist ungefähr 400,000). Für den Proportionalitätsfaktor findet Delbrück den Wert 0,005.

Nach der Idee von Moglich und Schön haben wir uns die Absorption eines $h\nu$ durch ein Molekul des Fermentes so vorzustellen, daß ein Elektron aus einem unteren Energieband in ein höheres Energieband hinaufgehoben wird. Das im unteren Energieband entstandene Loch bietet einem anderen, nicht angeregten Elektron Gelegenheit zu einem Quantensprung, sukzessiv wandert also dieses Loch an den oberen Rand des unteren Energiebandes (bzw. an den oberen Rand des besetzten Teiles dieses Energiebandes). Das in einem höheren Energieband erschienene Elektron wird seinerseits ebenfalls innerhalb sehr kurzer Zeit Quantenübergänge ausführen und dadurch an den *unteren Rand* jenes höheren Energiebandes wandern. Danach ergibt sich eine gewisse Verweilzeit, die schließlich dadurch beendet wird, daß das Elektron entweder zum unteren Energieband zurückspringt oder aber eine Umlagerung des Molekuls veranlaßt, die zur Inaktivierung führt. Die Herbeiführung dieser Umlagerung kann übrigens nach den Vorstellungen von Moglich und Schön genauer verständlich gemacht werden durch einen Vergleich mit den Prozessen, die an *Leuchtphosphoren* studiert worden sind. Hier wollen wir augenblicklich nur die Tatsache betonen, daß die Proportionalität der beiden Spektren durch dieses Modell offenbar eine sehr natürliche Erklärung findet: es wird ja ein von der Frequenz des absorbierten Lichtquants *unabhängiger* Zustand hergestellt, bevor zwischen Rückkehr in den Normalzustand oder Inaktivierung entschieden wird.

Die geringere Wahrscheinlichkeit, mit welcher die Absorption eines $h\nu$ zur Inaktivierung des Ursase-Molekuls führt, kann ferner, wie Delbrück bemerkte, auch die oben erwähnte Tatsache als verständlich und natürlich erscheinen lassen, daß bei *Bact. coli* nur ein kleiner Bruchteil der $h\nu$ -Absorptionen, welche in dem aus der Röntgen-Tötung berechneten Volum v_0 stattfinden, zur Tötung führt.

Versuchen wir andererseits die erläuterte Modellvorstellung anzuwenden auf die nicht-exponentielle Tötung von *Bacterium coli* durch 3132 \AA , so kommt man bei näherer Betrachtung zu dem Ergebnis, daß es ohne wesentliche Ergänzung oder Abänderung dieser Modellvorstellung kaum möglich sein dürfte, eine *Akkumulierung* der Wirkungen absorbierten Lichtquants *in der Form* zu erhalten, daß die Anregung von mehr als einem Elektron innerhalb eines Genmolekuls zu einem anderen Effekte führt, als von der Anregung eines einzelnen Elektrons zu erwarten wäre. Es scheint deshalb bei Aufrechterhaltung unserer Modellvorstellung nur folgende Deutung möglich zu bleiben. Die Wellenlänge 3132 \AA vermag (außer unmittelbaren Tötungen) auch gewisse nicht tötende, aber *vitalitätsvermindernde* Mutationen zu erzeugen. Ein *einmal* in diesem Sinne mutiertes Individuum bleibt lebensfähig, aber nach Erleidung von *zwei* derartigen Mutationen stirbt das

Individuum ab Diese Deutung ist einer *experimentellen Prüfung* zugänglich sollte sie sich künftig als falsch erweisen, so wurden wir unsere Vorstellung von der physikalischen Struktur der Gene wahrscheinlich erheblich komplizieren müssen

Für den oben erwähnten besonderen Effekt an der *Hefe* konnte man von der hier betrachteten Modellvorstellung aus folgende Deutung versuchen Wir nehmen an, es seien zwei (oder noch mehr) nah benachbarte Genmoleküle G' , G'' im Chromosom vorhanden mit der Eigenschaft, daß eine Mutation nur *eines* dieser Gene noch keine merkbare Schädigung hervorbringt, wohl aber die gleichzeitige Mutation beider Diese gleichzeitige Mutation beider Gene G' , G'' wird bei Anwendung von Röntgenstrahlen in erster Linie dann zustande kommen, wenn *in jedem von ihnen* eine Ionisierung geschieht Es möge nun ferner ein drittes Molekül N mit diesen beiden Genmolekülen G' , G'' in enger Verbindung stehen derart, daß eine in N geschehende Umlagerung sekundär G' und G'' zur gleichzeitigen Mutation veranlassen kann Eine in N stattfindende einzelne Ionisierung kann dann allerdings beide Gene G' , G'' zugleich zur Mutation veranlassen, aber häufiger werden *zwei* in den einzelnen Genen geschehende Ionisierungen den fraglichen Effekt hervorbringen Andererseits wird ein ultraviolettes Licht—quant die beiden Gene zur Mutation veranlassen können, sofern es eine geeignete Frequenz hat, um von dem Molekül N leicht absorbiert zu werden

Diese Vorstellung ist vielleicht nicht so willkürlich und unbegründet, wie sie zunächst erscheinen mag Man weiß nämlich, daß die das Gerüst der Chromosomen bildende Nukleinsäure in der Nähe der von Schreiber benutzten Linie 2540 \AA ein starkes Absorptionsmaximum hat Es konnte also sein, daß die erläuterte Vorstellung tatsächlich *ungefähr* den wirklichen Verhältnissen entspricht, und daß das Molekül N ein Nukleinsäure-Molekül ist

Jedoch läßt der gegenwärtige Stand unserer experimentellen Kenntnisse noch keine sichere Beurteilung dieser Fragen zu Die gemachten Bemerkungen sollten nur dazu dienen, zu zeigen, in welcher Richtung vielleicht eine ins Einzelne gehende Deutung der gefundenen Effekte versucht werden könnte, der Versuch, sich eine bestimmte Modellvorstellung zu machen, dürfte nützlich sein für die Anregung weiterer experimente in diesem interessanten und schonen Untersuchungsgebiet, welches auf eine *Zusammenarbeit* von Physikern und Biologen angewiesen ist, welches dem Biologen bedeutungsvollste Aufschlüsse verspricht, und welches dem Physiker Gelegenheiten zu vielseitiger Anwendung unseres atomphysikalischen und quantentheoretischen Wissens gibt

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THE DISPERSION OF THE ULTRASONIC VELOCITY IN LIQUIDS.

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§ 1 THE question of the existence of a dispersion of the ultrasonic velocity in liquids has in recent years been the subject of numerous investigations. Amongst the authors¹ Prof. Sir C. V. Raman and his school of physicists must be mentioned in the first place, because they have contributed many extremely important papers to this problem and to the related one of the fine-structure of the Rayleigh-line of light-scattering. Hence it gives me special satisfaction to have the opportunity of publishing some measurements on this question in the Raman-Jubilee Volume of these *Proceedings*. The results of my investigation are as yet rather meagre and bear on two substances only, but as all new measurements in this field may be of some help, I dare to publish this work even in its present imperfect state.

Experimental

§ 2 The method with some preliminary results has already been shortly described in a recent paper in *Helv. Phys. Acta*², it has now been somewhat improved and yields for the determination of the velocity $v = \lambda \cdot \Omega$ (λ = sound-wavelength, Ω = sound-frequency) in suitably selected liquids (e.g., water) an accuracy of a fraction of a permille.

(a) λ is measured by means of the usual method of the diffraction of light by sound waves, on which nothing further need be said.

On the other hand, some remarks must be made on what is generally considered as a serious source of error. This is the strong dependence on temperature of the sound-velocity, which may vitiate the results, especially if one uses very high frequencies (cf. below), where there is a marked absorption of the sound-energy. But it seems that this difficulty can be overcome to some extent by using a strong light source and sensitive photographic plates for taking the diffraction spectra. If the two measurements of v at the two frequencies are made in a sufficiently short time interval and if the

¹ We will cite only the latest papers: C. V. Raman and B. V. Raghavendra Rao, *Nature*, 1937, 139, 585, and 1938, 141, 242; B. V. Raghavendra Rao, *Proc. Ind. Acad. Sci.*, 1938, 7, 163, cf. also *Nature*, 1937, 139, 885; A. K. Dutta, *Phys. ZS.*, 1938, 39, 180; S. Parthasarathy, *Curr. Sci.*, 1937, 6, 55; B. G. Spakovskij, *Doklady*, 1938, 18, 109.

² R. Bär, *Helv. Phys. Acta*, 1938, 11, 472.

sound waves are only excited during the time of exposure of the photoplate, the corresponding change in temperature can be kept negligibly small

The *local* rise in temperature on the spot, where most of the sound energy is absorbed in the liquid, then gives, owing to the temperature gradient, rise to some sort of mirage, i.e., to a bending of the light-rays, which pass through this region. Hence this portion of the liquid is automatically eliminated from the measurements. If the sound waves are generated during a time interval, which is very much longer than the one which is necessary for photographing the spectra, this mirage is easily observed as a shaded wing on one side of the undiffracted line and similar weaker ones adjoining the diffraction-lines. Fig 1 shows the phenomenon as it is observed in benzene with a frequency of 18.75 MHz. It can be made to disappear by shielding off the portion of the liquid close to the sound-quartz. An analogous wing can also be generated by placing a brass-rod, which must only be a few degrees warmer than the liquid, for some seconds in contact with the glass wall of the vessel, on which the quartz is cemented. Conversely a wing on the opposite side of the line originates, if one puts a cooled rod in contact with the wall.

The phenomenon is very conspicuous in benzene and in acetic acid, whereas it is much weaker in water. Of course it is a hindrance to the wave-length measurements, this may be the reason why the accuracy of the results obtained with water is higher than that with many other liquids.

(b) Of the sound-frequencies used, the lowest one [$\Omega_1 = 7\,5088$ Mega-Hertz (MHz)] was exactly known, because it was generated by a quartz-controlled oscillator. The higher frequencies used ($22.5 \div 52.5$ MHz) were different for different liquids, but they were always chosen as high as was compatible with the sound-absorption of the liquid under investigation. This was done for the two reasons that, in this high frequency-range the experimental data are particularly meagre, and because a recent theory of Kneser³ seems to indicate that a dispersion effect may be easier to observe with high frequencies.

§ 3 All sound waves were generated with one and the same sound-quartz, which was ground for 7.5 MHz. When the quartz was excited in this fundamental tone, an oscillator O_1 was used, the frequency of which was kept at 7.5088 MHz by means of the above-mentioned *master-quartz*. A number of higher harmonics m_1, m_2, m_3, \dots of O_1 could then be detected with a sensitive wave-meter. When the sound-quartz was made to vibrate in an overtone, another oscillator O_2 was used, the harmonics n_1, n_2, n_3, \dots

³ H. O. Kneser, *Ann. d. Phys.*, 1938, **53**, 277.

of which could also be measured with this wave-meter As O_2 was *not* quartz-controlled, the mode of vibration of the sound-quartz could then in some measure be varied at will and different states could be reached, where some harmonic m_1 was equal to some other n_k The frequency Ω_2 of O_2 , with which the sound-quartz was then vibrating, is in this case $\Omega_2 = n_k/m_1$, $\Omega_1 = x \Omega_2$, where x = small rational number

Results

§ 4 The results for the two liquids, distilled water and benzene, are shown in Tables I and II and in the diagrams of Figs 2 and 3 respectively, where the value of the sound velocity (ordinate) is plotted against the value of the temperature T of the liquid (abscissa) What one really measures is of course not the wavelength itself but the distance of the diffraction spectra The factor for converting one magnitude into the other requires intricate measurements, which are not relevant for the present purpose Hence the very accurate new measurements of Seifen⁴ were taken as a basis, they yield for the sound velocity in water at 20° C a value of 1483.2 m/s With the corresponding conversion-factor all values of v for the three liquids were calculated

(a) *Distilled water*—Owing to the small sound absorption, measurements with very high frequencies are feasible in this liquid Consequently the comparatively high value of $x = 7$ can be used, which makes $\Omega_2 = 52.5$ MHz The results of Table I and Fig 2 show that in water in the interval 7.5 ÷ 52.5 MHz *no dispersion* is visible, the deviations from the curve are here

TABLE I
Sound Velocity in Dist Water

T	$v_{7.5}$	$v_{52.5}$
17.55° C	1475.9 m/s	1475.4 m/s.
17.95	76.9	77.2
19.12	80.3	80.3
19.56	81.9	81.7
20.62	84.4	85.1

⁴ N. Seifen, *ZS. f. Phys*, 1938, 108, 681.

particularly small and remain (with one exception) $< 0.3 \text{ m/s} = 0.2 \%$. These measurements may serve as a complement to those already published (R. Bär, *loc cit*)

Sound velocity in dist Water

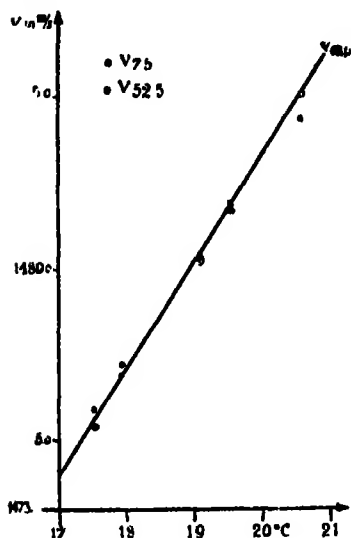


FIG 2

Sound velocity in Benzene

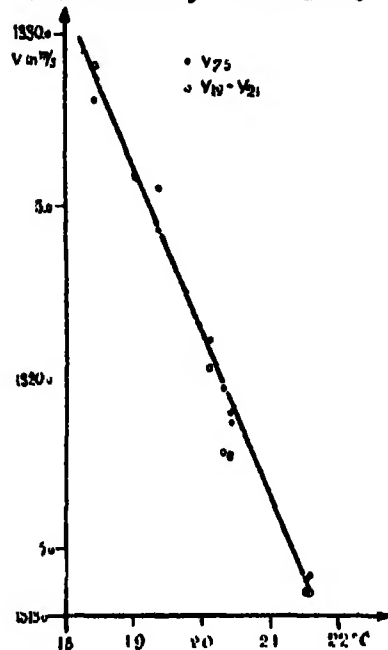


FIG 3

(b) *Benzene* —The rather high absorption prevents measurements above 21 MHz ($\alpha = 5/2, 8/3$ and $14/5$ were used) Again *no dispersion* is visible (*cf* Table II and Fig 3) It must be mentioned however, although it is not relevant in this connection, that the absolute values of the velocity are somewhat smaller (about 3 m/s) than those of the best new measurements. As no special care was taken to get really well-purified benzene, this does not seem surprising

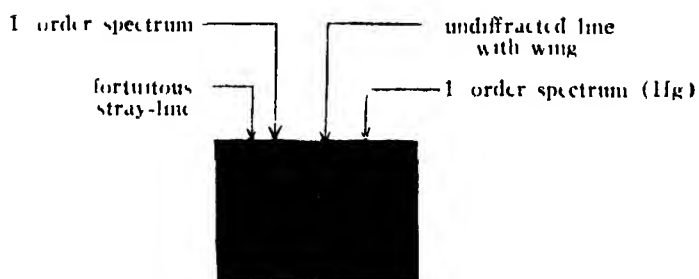


FIG. 1 - Wing-phenomenon in benzene at 1875 MHz

TABLE II
Sound Velocity in Benzene

T	Ω_s	$v_{\gamma s}$	v_{Ω_s}
18 44° C	21 0 MHz	1328 1 m /s	1329 1 m /s
19 36	„	24 3	25 5
20 12	18 8	21 1	20 3
20 31	20.0	19 7	17 8
20 41	„	18 7	17 7
20 42	„	19 0	17 8
21 52	21 0	13 7	14 1
21 56	„	14 2	13 7

Summary

§ 5 No dispersion of the ultrasonic velocity is found for water between $7.5 \div 52.5$ MHz and for benzene between $7.5 \div 21$ MHz

A STATISTICAL ANALYSIS OF TRENDS IN RESEARCH ON THE RAMAN EFFECT.

BY JAMES H HIBBEN

(From the Geophysical Laboratory, Carnegie Institution of Washington, Washington, D C)

IN view of the tenth anniversary of the discovery of the Raman effect, it appears appropriate to make a statistical analysis of the numerous publications in this field. It is useful to determine, for example, whether the interest in this discovery has passed through a maximum—as have many other chemical and physical developments—and then waned. One method of determining this would be to plot the number of published articles on the subject or the number of manuscript pages as a function of time. An accurate determination of the number of pages is not practicable. The number of separate publications, however, can be estimated and it is found that there are nearly seventeen hundred of them over a ten-year period. The rate of publication is shown in the graph in Fig 1.

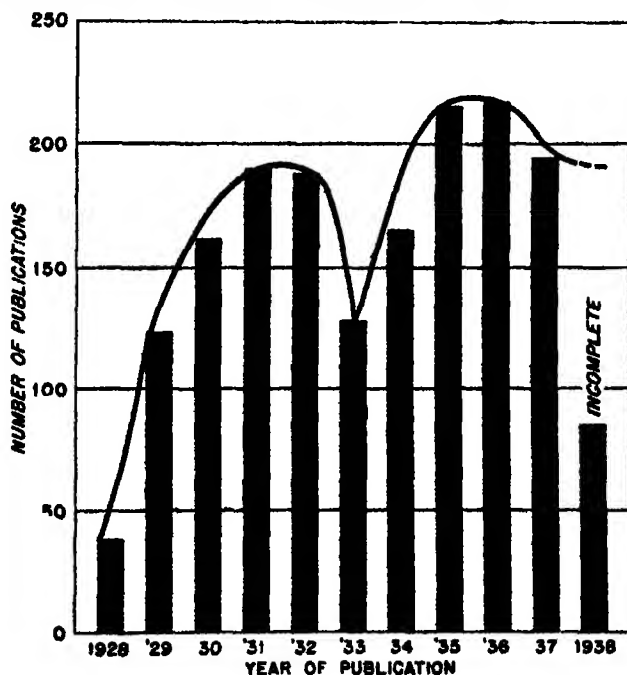


FIG. 1.

The number of publications per annum on the subject of the Raman effect.

This figure illustrates the very rapid rise in interest in the subject and the sustaining of this interest over a relatively long period. On the other hand, the graph exhibits a peculiarity which appears to be very significant and not fortuitous. This is the rather sudden drop in the publication rate which reaches a minimum in the latter part of 1933. With regard to this behaviour there are several comments which may be of interest.

The first of these is that an increase in the average length of papers might cause a diminution in the average number, but would not account for the second rise in the curve. Furthermore, a generous sampling of publication-length indicates that the average paper is about five pages in length and this has not altered greatly with time.

The possibility of the effect of the depression in the United States—which reached a maximum in 1932—on research funds, endowments and scholarships would occur to the average American. Such an effect would be a delayed one and would ostensibly account for both the diminution and the subsequent increase in the publication rate. However, a closer examination of all the pertinent facts shows that this hypothesis is, at best, only partially tenable. The over-all decrease in 1933 from the general average is 30 per cent, but in the United States where the financial situation was more acute at this particular period than abroad, it reached a value only slightly lower, namely 33 per cent, while in Germany, combined with Austria, the reduction was 47 per cent. Part of the latter reduction can undoubtedly be attributed to the known diminution in fundamental research in Germany. Finally, it can be shown that the world-wide recession in all types of chemical and physical articles in 1933 amounted to but five per cent. This seems to confirm the view that the drop in the rate of publication in 1933 on the subject of Raman spectra is significant, that it was not greatly affected by economic conditions, and that the length of articles played no obvious rôle.

These factors having been considered, the next step is to examine the possibility of a real drop in interest in the Raman effect following the fading of the first bloom of novelty. This undoubtedly enters into the picture and is probably partially responsible for the dip in the curve. However, if this is accepted as an interpretation, the re-awakening of interest after 1933 must also be explained. This becomes clear to some extent when it is remembered that the Raman effect began as a step-child of physics, but as time progressed it became the adopted son of chemistry.

It was during the period from 1932 to 1934 that the purely theoretical emphasis changed from an explanation of the origin of the Raman effect to the correlation of that effect with the modes of atomic vibration. Furthermore,

it was during this period, that there was an increased realization of the applicability of the Raman effect to structural and constitutional problems

All the influences thus outlined may collectively play a rôle in the production rate, but as a complete explanation none of them leaves one with a feeling of consummate satisfaction. Nevertheless, these data indicate a wide and sustained interest in the Raman effect which will apparently continue for an indefinite period

Another item of interest is the extensive distribution of research work on this subject. This may be determined from the number of publications whose experimental data or theoretical conclusions originate in various localities. This is quite distinct from nationality of the author or the place of publication. These results are shown in Fig 2

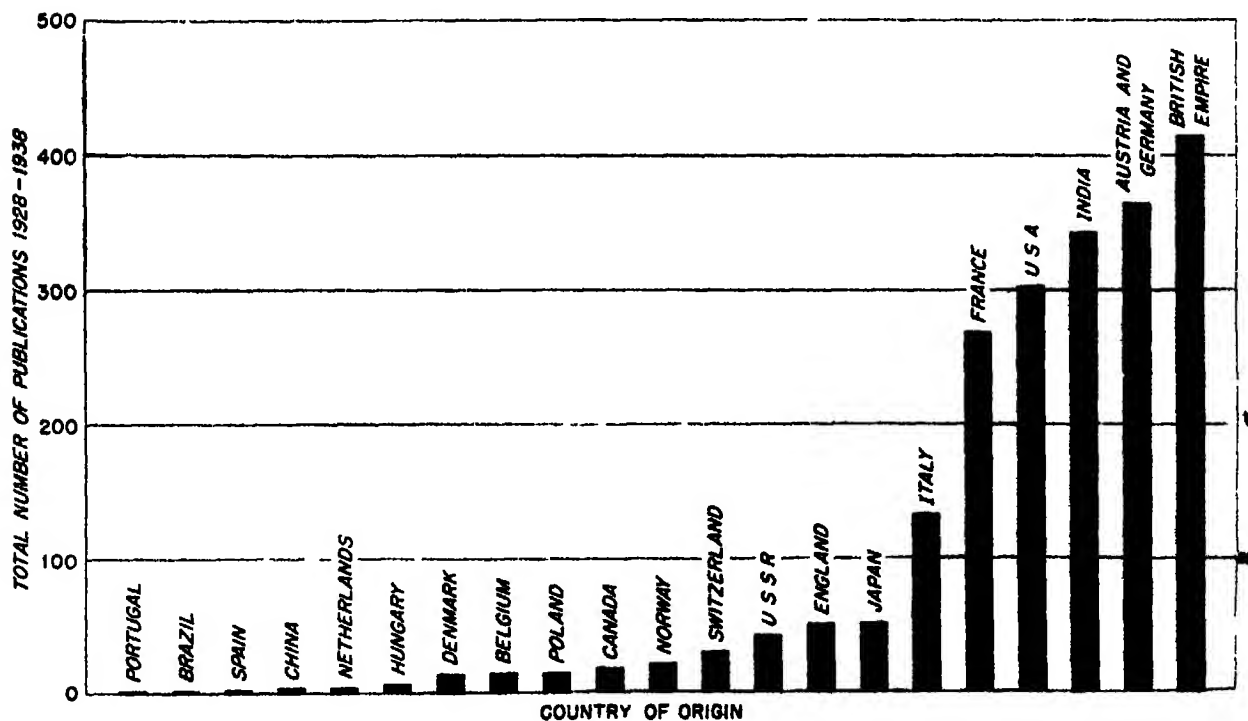


FIG 2.

The geographical distribution of research on the Raman effect

This figure indicates that most of the work is being carried out in the British Empire (India, England and Canada), Germany and Austria (most of the publications of this combination originated in erstwhile Austria), the

United States, France, Italy, and the remainder in some fifteen other countries. For an individual geographical unit, India, as might be expected, is the most prolific producer of research on the Raman effect. The German-Austrian and Italian outputs differ from the others in resulting principally from the efforts of a relatively few individuals in those countries rather than from the efforts of groups of workers as in other countries.

The next items to consider from a statistical point of view are the trends indicated by the number of compounds investigated, the number of times each has been studied, and the type of compounds. From 1928 to September 1938 there have been examined 2,101 different organic compounds and 385 different inorganic substances, or a total of 2,486, discussed in 1,700 publications. The list of new compounds investigated is increasing at the rate of approximately 20 per cent per annum taking the past three years as a criterion. Furthermore, previous investigations are being repeated. For example, it is found that the number of publications on the Raman spectra of benzene increases at the rate of 13 per cent per annum, if the one hundred and twenty-five papers on this substance in 1935 are used as a base level.

The type of compound studied is also of interest. For the purpose of presentation these compounds are divided into two classes, organic and inorganic, and each of these, in turn, is subdivided into categories according to broad constitutional characteristics. The results obtained from the first class are shown in Table I, and are given in terms of the relation of any particular category to the largest category, namely, the halogen derivatives of aliphatic hydrocarbons. In making comparisons it should be noted that in some cases the hydrocarbons and all derivatives are lumped into one unit, while in others there is additional classification. This is done when the number in different classes would be rather insignificant.

It is noticeable from Table I that the halogen and carbonyl derivatives of saturated aliphatic hydrocarbons are more popular sources of Raman spectra than the hydrocarbons themselves. Probably this is because of the physical properties of the earlier members of the hydrocarbon series. On the other hand, the monosubstituted aromatic hydrocarbons, such as toluene, have been investigated much more frequently than any of the other derivatives. With the di- and tri-substituted compounds, however, the reverse is true and there is a diminishing popularity with increased substitution. This is easily understandable, inasmuch as the greater the complexity of the molecule the more difficult it is to allocate the Raman spectra properly, and the less clearly defined are the results.

TABLE I

Relative Number and Kind of Compounds Investigated

*Compounds	Relative No	Compounds	Relative No	Compounds	Relative No.
Aliphatic hydrocarbons	32	Aliphatic olefins	26	Acetylenic hydrocarbons	15
Halogen derivatives	100	Halogen derivatives	21	Halogen derivatives	1
Alcohols and ethers	67	Alcohols and ethers	7	Alcohols and ethers	9
¹ Carbonyl derivatives	100	Carbonyl derivatives	18	Carbonyl derivatives	1
Cyano compounds	16	Cyano compounds	4		
² Sulfur compounds	16				
³ Nitrogen compounds	35	Nitrogen compounds	4		
Metallo compounds	6				
⁴ Cyclic hydrocarbons	37	⁴ Polycyclic hydrocarbons	12	Heterocyclic nitrogen compounds	18
Cycloolefins	17	Heterocyclic polycyclic compounds	16	Heterocyclic oxygen and nitrogen or sulphur compounds	6
Terpenes	30	Heterocyclic alcohols and ethers	9		
<i>Benzene and Monosubstituted Derivatives</i>		<i>Disubstituted Derivatives</i>		<i>Trisubstituted Derivatives</i>	
Benzene and alkyl derivatives	66	Alkyl derivatives	9	Alkyl derivatives	4
Halides	17	Halides	24	Halides	12
Alcohols and ethers	9	Alcohols and ethers	10	Alcohols and ethers	5
Carbonyl compounds	28	Carbonyl compounds	13		
Cyano compounds	4	Cyano compounds	4	Cyano compounds	1
Sulfur compounds	2	Sulfur compounds	1		
Nitrogen compounds	15	Nitrogen compounds	16	Nitrogen compounds	4
Metallo compounds	1				

* The comparison between the relative numbers of compounds is made by assigning a value of 100 to the halogen derivatives

¹ Carbonyl includes acids, aldehydes, ketones, esters, etc

² Includes thioethers and mercaptans

³ Includes amines, amides, nitrates, etc

⁴ Includes all derivatives not listed elsewhere

It can be seen, therefore, that when a particular kind of compound has been examined or re-examined more frequently than others, there is usually some good reason for it. The interest in benzene has continued because it represents a characteristic class of compounds whose fundamental vibrations are not easily determined and whose symmetry is important. Carbon tetrachloride, which is equally important for the same reason, was re-examined with considerable frequency until the last three years, but now has only half the percentage increase that benzene possesses. This is because the symmetry (T_d) and fundamental vibrations have been determined. The continuing interest in this compound is now practically confined to the Fermi resonance effect and the influence of temperature. The number of studies on the terpenes is also out of proportion because of the interest in their chemical constitution as determined by the Raman effect. In general, the present trend with organic compounds is toward comparative determination of constitution and toward the precise determination of structural configuration through the symmetry characteristics of the molecules.

In the field of inorganic chemistry there are also preferences among the compounds studied. These are shown in Table II, which includes the principal types of compounds.

TABLE II
Relative Number and Kind of Some Inorganic Compounds Investigated

¹ Compounds	Relative No	² Compounds	Relative No	Compounds	Relative No	Compounds	Relative No
Nitrates	100	Water	100	Ammonia	32	Sulfuric acid	48
Sulfates	62	Ice	7	Carbon dioxide	32	Nitric acid	39
Carbonates	23	Diamond	10	Hydrogen	23	Hydrochloric acid	23
Acids	74	Silica	33	Oxygen	22	Hydriodic acid	14
Hydroxides	9	Carbon disulfide	46	Nitrogen	19	Perchloric acid	11
				Phosphine	7	Orthophosphoric acid	8
				Chlorine	5		

¹ Comparison made considering the nitrates as 100.

² Comparison made for all pure compounds considering water as 100.

Of all the types of inorganic compounds examined most freely, the nitrates lead the rest. These represent the nitrates of some twenty elements headed by sodium and the ammonium ion. Ammonium nitrate has been

frequently employed because it affords a means of studying both anion and cation simultaneously Both nitrates and sulfates have been frequently investigated as a corollary to experiments on the constitution of sulphuric and nitric acids As considerable light can be thrown on the behaviour and structure of these acids and their derivatives by means of the Raman effect, this accounts for the exceptional interest in acids in general and in these two acids in particular

The only carbonate examined frequently is calcium carbonate as calcite or aragonite This is because of the physical properties of the compound, the need to determine the Raman effect as related to the symmetry of a molecule of this type, and because of the lattice vibrations present The number of papers on carbon disulphide is also out of proportion in relation to the other compounds This may be attributed to the fact that it is a borderline compound between organic and inorganic chemistry and because of the splitting of frequencies in this substance due to coupling

There is fair uniformity among the gaseous substances relative to the frequency of investigation This is partially because an author usually discusses several gases at the same time Chlorine, along with phosphine, suffers a lack of attention for obvious manipulative reasons

One of the most interesting features of the entire table is the demonstration of the remarkable interest in water There are at present some eighty-eight separate publications on this subject Water has long been known to be an abnormal substance, and it is not surprising that Raman spectra have been frequently employed to study its behaviour under different conditions Water is of interest in itself because it represents the type of molecule consisting of three atoms having a non-linear configuration, it is the nearest known universal solvent, and it exhibits in a relatively high degree the phenomenon of intermolecular coupling It is this last feature which has stimulated much of the research on water and which is demonstrable by means of the Raman effect

Summary

There have been outlined in this presentation, the trends, during a ten-year period, in interest in the Raman effect as a function of time and geographical distribution The interest in particular types of organic and inorganic compounds has been evaluated, and the reasons for preferential treatment of certain classes and compounds have been discussed briefly

SPECTRES RAMAN ET SPECTRES D'ABSORPTION INFRAROUGE DE COMPOSÉS OÙ L'AZOTE EST TÉTRACOORDONNÉ

PAR MME MARIE FREYMANN ET MR RENÉ FREYMANN
(Laboratoire du Professeur Cotton, à la Sorbonne Paris)

Resume

Les auteurs ont examiné les spectres Raman et les spectres d'absorption dans le proche infrarouge (0,8 à 1, 2μ) de composés où l'azote est tétracoordonné. Ils comparent leurs résultats à ceux d'autres auteurs. Les conclusions suivantes en résultent.

1°—Pour les solutions aqueuses peu concentrées de tous les composés où l'azote est tétracoordonné, les fréquences caractéristiques du groupement NH sont absentes ou extrêmement faibles.

2°—Pour les mêmes substances à l'état solide, (ou les solutions aqueuses très concentrées) de larges bandes apparaissent, elles sont nettement déplacées vers les basses fréquences par rapport aux bandes correspondantes de l'azote trivalent.

La première de ces conclusions a été vérifiée pour les sels d'ammonium, pour les chlorhydrates d'amines, les aminoacides et les complexes aminés du cobalt, du cuivre et du platine.

C'est en se complétant mutuellement que les spectres de diffusion Raman et les spectres d'absorption infrarouge ont permis un développement rapide de nos connaissances sur la structure moléculaire. En général, ces travaux ont porté sur l'ensemble du spectre et la recherche des divers modes de vibration, cependant, nous allons essayer de montrer que l'étude de certaines vibrations particulières des molécules fournissent également d'utiles renseignements sur leur structure.

Les amines secondaires et primaires, l'ammoniac (substances renfermant dans leurs molécules des groupements NH, NH^2 ou NH^3 , où l'azote est trivalent), présentent une ou plusieurs fréquences Raman et infrarouges, très intenses, assez fines, voisines de $3\,300\text{ cm}^{-1}$ environ. Ces fréquences varient peu avec la nature des groupements attachés à NH ou NH^2 . Aussi peut-on, en première approximation, les attribuer à la vibration de valence.

$N \rightarrow H$ et les désigner par ν (NH) Les 1^{er}, 2^{ème}, 3^{ème}, ... harmoniques infrarouges seront désignés par 2ν (NH), 3ν (NH), 4ν (NH),*

Nous nous proposons d'examiner ce que deviennent ces fréquences pour les composés où l'azote n'est plus trivalent mais tétracoordonné, nous insisterons plus particulièrement sur les travaux effectués au laboratoire du Professeur Cotton, soit sur le 2^{ème} harmonique 3ν (NH) — vers $1,04\mu$ environ —, soit sur les fréquences Raman fondamentales correspondantes

Résumons dès maintenant les conclusions essentielles

1°—Pour les composés de l'azote tétracoordonné, en solution aqueuse assez diluée, il semble que toute fréquences NH de valence disparaisse (fondamentaux et harmoniques) (13, 6, 7, IIbis),

2°—Pour les mêmes composés à l'état solide (ou en solution très concentrée) les fréquences ν (NH) voisines de $3\cdot300\text{ cm}^{-1}$ n'apparaissent pas, elles sont remplacées par des bandes très larges de plus basse fréquence $3\ 000\text{ cm}^{-1}$ environ (ν (NH)),

C'est notamment aux beaux travaux d'Ananthakrishnan que l'on doit cette dernière observation

I Sels D'Ammonium

Considérons une solution ammoniacale contenant 20 gr de NH^3 pour 100 cm³ de solution, le spectre d'absorption dans le proche infrarouge présente plusieurs composantes dont la plus intense est voisine de $1,04\mu$, ces composantes correspondent au 2^{ème} harmonique (3ν (NH)) des fréquences voisines de $3\cdot300\text{ cm}^{-1}$. Au contraire, une solution de chlorure d'ammonium, de même teneur en NH^3 , ne montre pas de bande correspondante (13, 6, IIbis)

Ce résultat peut être illustré par l'expérience suivante

Dans les mêmes conditions expérimentales, trois spectres ont été enregistrés, sous une épaisseur de 2 cm pour 1°) une solution d'ammoniaque 12 N, 2°) la même solution partiellement neutralisée par l'acide chlorhydrique 3°) la même solution renfermant un excès d'acide. On voit sur la figure I† que la bande 3ν (NH) disparaît graduellement au fur et à mesure que l'azote passe de la valence 3 à la coordinence 4. C'est cet effet que nous avons désigné par "phénomène de dissimulation pour l'azote tétracoordonné"

* Nous ne parlerons pas ici des fréquences de déformation δ (NH) que nous n'avons pas étudiées

† Sur cette figure, les longueurs d'onde sont portées en abscisse, les déviations du galvanomètre en ordonnée. Ces courbes reproduisent les enregistrements directs, obtenus à l'aide d'un spectromètre enregistreur à réseau et à cellule thalofide, cette cellule sensible de $0,8$ à $1,2\mu$, à un maximum de sensibilité vers $1,0\mu$ (4)

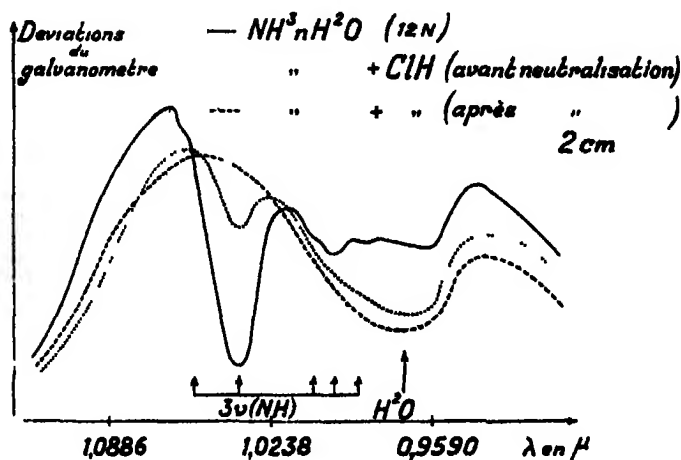


FIG 1

L'étude que nous avons faite (6) des spectres Raman de solutions peu concentrées a paru confirmer les données de l'infrarouge. Pour une solution d'ammoniaque les raies Raman sont très intenses, au contraire, pour une solution de NH_4Cl de même teneur en NH_3 (10, 5 gr pour 100 cm³ de solution), les bandes de l'eau apparaissent seules avec netteté.

En désaccord apparent avec nos résultats, les recherches sur l'effet Raman de divers auteurs (1, 12, 14, 15, 17, 18, 20) ont conduit aux conclusions suivantes : 1° Pour les composés à l'état solide les raies $\nu(\text{NH})$ voisines de 3 300 cm⁻¹ n'apparaissent pas. Mais elles sont remplacées par diverses bandes très larges, comprises entre 2,800 et 3 200 cm⁻¹ environ. Nous désignerons ces bandes par $\nu(\text{NH})$, pour rappeler leur présence dans le solide. 2° Pour des solutions aqueuses très concentrées (12N) de nitrate d'ammonium, Rao et Rao (19) ont signalé des raies Raman très larges et peu intenses, voisines de 3 100-3 200 cm⁻¹.

* *

Nous avons alors recherché si, pour de fortes concentrations, il n'existe pas, dans le proche infrarouge, de faibles bandes harmoniques de $\nu(\text{NH})$, nous avons étudié des solutions très concentrées et des sels fondus.

Comme le montre la fig 2, une large bande apparaît, vers 1,06μ ‡ pour le nitrate d'ammonium fondu (160° C)

‡ Cette bande est donc déplacée vers les basses fréquences par rapport à celles de l'ammoniaque.

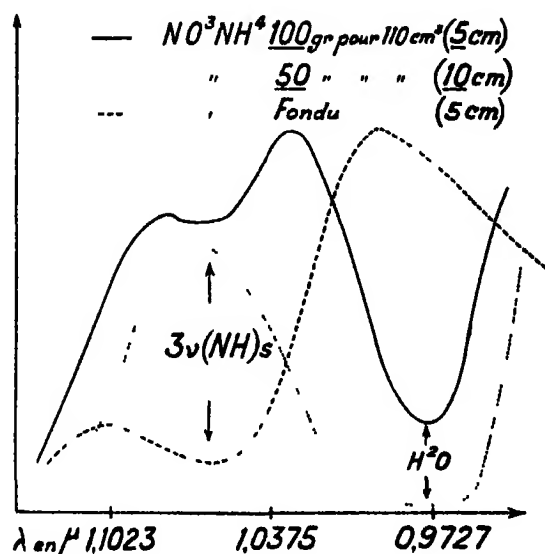


FIG 2

La même bande existe pour une solution aqueuse de nitrate d'ammonium très concentrée, examinée sous 5 cm d'épaisseur (100 gr de sel pour 110 cm³ de solution) Mais cette bande disparaît complètement pour une solution diluée de moitié, examinée sous une épaisseur double (Fig 2) Bien que la quantité de sel placée sur le trajet de la lumière soit la même dans les deux cas, la dilution fait disparaître la bande de 1 06μ. Il semblerait donc que cet effet soit lié à la dissociation



* * *

On peut alors se demander si la large bande de 1 06μ correspond au 2ème harmonique des fréquences Raman $\nu(\text{NH})_3$, s'il en est ainsi, ces fréquences Raman doivent disparaître également par dilution, ce qui expliquerait le désaccord entre les expériences de divers auteurs (sur des solutions concentrées) et les nôtres (relatives à des solutions assez diluées) Bien que cette façon de voir nous paraisse très vraisemblable, nous ne nous prononcerons pas encore de façon définitive, attendant les résultats d'expériences en cours d'une part sur l'effet Raman, d'autre part, en collaboration avec M Yeou Ta, sur la région infrarouge comprise entre 1,2 et 2 μ environ, des expériences sont également faites par Mr P Barchewitz, entre 0 6 et 0 9 μ. Nous affirmerons simplement ici la disparition très rapide de la faible bande de 1 06 μ, lors de la dilution

* * *

Pour montrer que la disparition des bandes caractéristiques du groupement (NH) n'est pas propre seulement aux sels d'ammonium, nous avons étudié divers autres types de composés où l'azote est tétracoordonné. Nous examinerons seulement ici la disparition de $\nu(\text{NH})$, sans étudier la possibilité de l'apparition de faibles bandes $\nu(\text{NH})$, pour les solutions très concentrées. Des difficultés expérimentales ne nous permettent pas actuellement de conclure au sujet de ces dernières et nous nous proposons de reprendre cette question.

II Chlorhydrates D'Amines

Les solutions diluées de chlorhydrates d'hydrazine, d'hydroxylamine, de diaminophénol etc. présentent, dans l'infrarouge, le même effet que les sels d'ammonium. Les bandes voisines de 1.04μ , très intenses pour $\text{NH}^3 \text{NH}^2$, s'affaiblissent déjà fortement pour $\text{NH}^3 \text{NH}^{3+} \text{Cl}^-$, elles disparaissent presque totalement pour $^-\text{Cl}^+ \text{H}^2\text{N} \text{NH}^{3+} \text{Cl}^-$ (13, 6, IIbis).

Les spectres Raman des solutions de chlorhydrates confirment cette disparition (3, 6), toutefois, pour les solutions suffisamment concentrées, nous ferons les mêmes restrictions que pour les sels d'ammonium (possibilité de l'existence de faibles bandes $\nu(\text{NH})$).

III Composés Amphotères

On peut rapprocher ces recherches sur les chlorhydrates de celles effectuée par l'un de nous, en collaboration avec Mr P. Rumpf (5, 6, IIbis), sur les aminoacides amphotères (glycocolle, taurine, paratoluènesulfamide). Le spectre infrarouge d'une solution aqueuse de glycocolle ne présente pas la bande $3 \nu(\text{NH})$. L'azote doit donc être tétracoordonné et le glycocolle sera formulé $^+\text{H}^3 \text{N} \text{CH}^2 \text{COO}^-$. Par contre, cette bande est très intense pour le glycocollate de sodium, on représentera donc cette substance par $\text{NH}^3 \text{CH}^2 \text{COO}^- \text{Na}^+$ (où l'azote est trivalent).

Les résultats précédents, relatifs à l'infrarouge, sont en parfait accord avec les importants résultats qu'Edsall a obtenu, indépendamment de nous, sur l'effet Raman des aminoacides en solution (3). On voit que les méthodes spectrales s'accordent pour confirmer, avec simplicité, les conclusions fournies par d'autres méthodes physico-chimiques sur la structure des aminoacides.

IV Complexes Amminés Du Cobalt, Du Cuivre, Du Platine

On aurait pu objecter que dans les exemples précédents ce sont $(\text{NH}^4)^+$ ou $(\text{NH}^3)^+$ que l'on étudie, et non le groupement NH^3 . Il n'en est pas de même pour les complexes amminés du cobalt et du cuivre que nous avons étudiés avec Mr le Professeur Job (13) ou ceux du platine, examinés par Mr. J. P. Mathieu et l'un de nous (10). Comparons, par exemple, le spectre

infrarouge d'une solution aqueuse de $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}^2$ et une solution ammoniacale contenant la même quantité de NH_3 , pour cette dernière $3\nu(\text{NH})$ est très nette, alors qu'elle est beaucoup plus faible pour la première (6, IIbis)

La même remarque a été faite (6, IIbis) pour $[\text{Cu}(\text{NH}_3)_4]\text{Cl}^2$, complexe imparfait peu dissocié en solution. Par contre, un complexe très imparfait (nitrate d'argent ammoniacal) montre nettement $3\nu(\text{NH})$

La fig 3 confirme la disparition de $3\nu(\text{NH})$ pour un complexe amminé du platine. Une solution aqueuse à 50 % de $[\text{Pt py}_2(\text{NH}_3)_2]\text{Cl}^2$, renfermant 3,7 % de NH_3 , ne montre pas $3\nu(\text{NH})$, alors que cette bande existe pour une solution ammoniacale à 2 % seulement

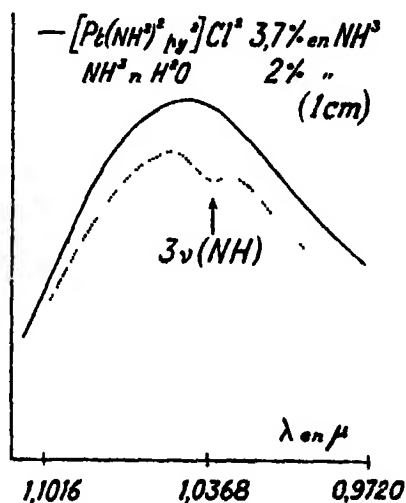


FIG 3

d'après J P Mathieu et M Freymann (10).

En ce qui concerne l'effet Raman des complexes, rappelons notamment les travaux effectués par Mr J P Mathieu, seul, ou en collaboration avec l'un de nous (16, 10). Ils s'accordent parfaitement avec les données de l'infrarouge, toutefois, il ne faut pas exclure la possibilité de l'existence de $\nu(\text{NH})$, pour ces complexes à l'état solide de nouvelles recherches sont nécessaires

V Conclusion

L'existence du phénomène de dissimulation permet, dans certains cas, l'étude de molécules dont la structure est encore discutée. C'est ainsi que nous avons montré (6) que les solutions aqueuses d'ammoniaque ne doivent pas être formulées NH_4OH mais que la majorité des molécules est sous la

forme $\text{NH}^+\text{NH}^+\text{O}$ La structure de certains aminoacides compliqués pourrait également être établie ainsi

D'autre part, il semble que toute interprétation théorique détaillée serait actuellement prématurée, faute de données expérimentales. Cependant, il nous paraît intéressant de rapprocher cette étude sur le groupement NH de celles faites sur le groupement OH des alcools, acides, oximes, etc., (4,8,9,11.) Rappelons que lorsque le groupement OH est libre (vapeur d'alcool par exemple) on observe une bande fine dont le fondamental est voisin de 3600 cm^{-1} (nous la désignons par $\nu(\text{OH})_v$ pour rappeler son existence dans la vapeur). Quand le groupement OH est engagé dans une liaison hydrogène (soit intramoléculaire comme dans l'aldéhyde salicylique, soit intermoléculaire comme dans l'association moléculaire des alcools), une bande très large apparaît vers 3400 cm^{-1} , cette bande se reproduisant dans ces composés à l'état solide nous la représentons par $\nu(\text{CH})_s$. Or, en étudiant avec Mr Guéron (11) des solutions chlorhydriques d'alcool—(l'éther, l'acetone, le dioxane ont été également examinés)—nous n'avons retrouvé, dans le proche infrarouge, ni la fréquence $3 \nu(\text{OH})_v$, ni la fréquence $3 \nu(\text{OH})_s$. Il nous semble donc intéressant d'établir le parallèle suivant entre les résultats relatifs à l'oxygène et à l'azote

OH libre	OII associé ($\text{O}-\text{H} \leftarrow \text{O}$)	Solutions chlorhydriques (non-ionisées ?)
3600 cm^{-1} (fine)	3400 cm^{-1} (large)	Bandes OH très faibles ou absentes
NH pour l'azote trivalent	NH pour l'azote pentavalent	Solutions chlorhydriques ionisées (pour l'azote pentavalent)
3300 cm^{-1} (fine)	3000 cm^{-1} (large)	Bandes NH très faibles ou absentes

* *

On voit que si un certain nombre de faits expérimentaux sont établis, il reste encore beaucoup à faire pour étudier des problèmes qui intéressent tout particulièrement la théorie de la liaison coordinative. De telles recherches montrent la nécessité de confronter ces deux techniques intimement liées, Les spectres de diffusion Raman et les spectres d'absorption infrarouge.

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SOME REMARKS ON RECIPROCITY.

BY MAX BORN

As I had the privilege of collaborating with Sir C V Raman in his Institute for a period of six months in 1935-36 I have a great desire to show my admiration of his discoveries and my appreciation of his unceasing efforts for the advancement of Indian Science by contributing to this volume of homage devoted to papers on scattering of light and Raman effect. But since the olden days when I did some work in this field¹ it has developed so marvellously that it has become the domain of a class of specialists with whom a 'general practitioner' of physics cannot compete. Therefore I shall content myself with presenting a few remarks of a very general nature, about the difficulties which theoretical physics encounters when dealing with the nature of light and ultimate particles.

These difficulties appear formally as the infinite self energies of the particles, but the real problem is the theoretical derivation of the ratio of the masses of these particles (Electron Yukon Neutron-Proton as about 1 : 200 : 1850), and this problem is certainly closely connected with that of the fine structure constant $\frac{\hbar c}{e^2} = 137$. At present separate wave functions are introduced for each kind of particle, containing the proper mass as coefficient. This state of affairs is highly unsatisfactory, and it is generally agreed that a comprehensive theory must lie behind it, containing only one

¹ My contribution to the classical theory of scattering consists of an investigation (*Verh d Deutsch Phys Ges*, 1917, p 243, 1918, p 16) on the depolarisation of light scattered from anisotropic molecules. This depolarisation effect had already been derived by Gans (*Ann d Phys*, 1912, (4), 37, 881) for colloidal particles by treating these as conducting ellipsoids. I showed that the effect was a general consequence of the fact that in any anisotropic polarisable system, the polarisation vector excited by an electric field is not parallel to the field vector, it can, therefore, be expected also for anisotropic molecules and used for the determination of the anisotropy.

When quantum theory developed, Smekal (*Naturw*, 1923, 11, 874) predicted the existence of a new kind of scattering with change of frequency using the idea of light quanta (photons). Kramers and Heisenberg (*Zeitsch f Phys*, 1925, 31, 181) derived this effect by modifying the usual dispersion theory according to Bohr's correspondence principle. When Heisenberg, Jordan and myself developed the new quantum theory (*Zeitsch f Phys*, 1926, 35, 557) we applied the matrix formalism also to this problem and confirmed the formula of Heisenberg and Kramers. This incoherent scattering of light is the effect which Raman and Krishnan (and Landsberg and Mandelstam) found experimentally, and I am proud that my work had some connection with this fundamental discovery.

constant This constant may be considered either as a universal length a , momentum b , energy ϵ or mass m , as one has

$$(1) \quad ab = \hbar, \quad b = mc, \quad \epsilon = mc^2$$

It is further generally agreed that the universal length which determines the breakdown of the present theories² is of the order 10^{-13} cm, which is that of the 'radius' of the electron and simultaneously of all nuclei, presumably

one has $a = \frac{e^2}{m_0 c^2} = \frac{\hbar}{137 m_0 c} = 2.81 \times 10^{-13}$ cm, where m_0 is the mass of the electron, therefore $b = 137 m_0 c$, $\epsilon = 137 m_0 c^2$

I have made an attempt to introduce the absolute constant in quite a different way, namely as an absolute electromagnetic field E or potential ϕ , this is, of course, also equivalent to one of the other constants, on account of the equations

$$(2) \quad E = \frac{e}{a^2}, \quad \phi = \frac{e}{a}$$

It was possible to construct a non-linear electrodynamics³ which led to the existence of point charges with finite self-energy. But this construction is not uniquely determined, and it was not possible to find an additional principle to render it unique. Furthermore, the quantization of the non-linear field equations did not give satisfactory results concerning the existence and mass of particles. Therefore, I do not consider this way as promising at present. Recently, it has been shown by Dirac⁴ and Pryce⁵ that the appearance of infinite self-energy of point charges can be avoided by an alteration of the definitions of force, momentum and energy as given in Lorentz's classical theory of the electron. These new conceptions are in accord with the field equations and have no influence on any observable fact. Though this result is not a solution, but rather an evasion of the problem of explaining the elementary masses, it shows that the difficulties connected with the self-energy cannot be used as indicators.

² The question of the limits of the present theories has been recently discussed in two interesting papers by Heisenberg (*Ann d Phys*, 1936, (5), 32, 20; *Zeitsch. f. Phys*, 1938, 110, 25). In the first of these papers he discusses the 'universal length' appearing in the theories of elementary particles. In the second publication he has accepted the view suggested by myself (in the papers quoted below) that we have primarily to do with an absolute momentum.

³ M. Born, *Nature*, 1933, 132, 970; *Proc Roy Soc.*, (A), 1934, 143, 410; M. Born and L. Infeld, *Nature*, 1933, 132, 282, 940; *Proc Roy Soc.*, (A), 1934, 144, 425, 1934, 147, 522, 1935, 150, 141.

⁴ P. A. M. Dirac, *Proc Roy. Soc., London*, (A), 1938, 167, 148.

⁵ M. H. L. Pryce, in print. I have to thank Mr. Pryce for allowing me to read the manuscript.

One feature of this attempt at generalised electrodynamics seems to survive, namely the non-linearity of the equations. For it is very difficult to conceive a merging of the different wave equations of the elementary particles (including photons and neutrinos) into one comprehensive theory if this theory is to be linear. But there are very few experimental indications of deviations from the accepted linear laws. The relativistic quantum theory of the electron seems to hold up to the highest energies occurring in cosmic rays⁶. The structure of nuclei can be treated even without considering relativistic effects owing to the high mass of the constituent particles. The only deviations seem to occur in the case of fast Yukons which do not obey the laws predicted by the linear theory⁷.

Therefore, we have no other means of discussing possibilities of future development than purely theoretical considerations. The only natural and unique way of introducing non-linearity into a field theory is that used by Einstein in his theory of gravitation, namely the postulate of general invariance which leads us to consider space-time as non-Euclidean, or 'curved'. But Einstein's theory has to do with very small curvatures, imperceptible in regions of laboratory dimensions. It is also clear from the smallness of the gravitational constant that cosmological curvature has nothing to do with atomic effects. These are bound to extremely small linear dimensions, of the order a , introduced above. But as the small length a , according to (1), is associated with a large momentum $b = \frac{\hbar}{a}$, I have suggested that the domain of the elementary particles has to be considered from the standpoint of momentum space in which a non-linear geometry with small curvature reigns.

This idea, which I have called the 'principle of reciprocity' is based on the fact that in quantum mechanics space-time and momentum-energy are symmetrically related by commutation rules of the form

$$(3) \quad -i[x, p] = xp - px = i\hbar$$

so that we can either take the x as 'diagonal' (c -numbers, according to Dirac's expression) and the p as the operators $\frac{\hbar}{i} \frac{\partial}{\partial x}$ or, *vice-versa*, the p as 'diagonal' and the x as $-\frac{\hbar}{i} \frac{\partial}{\partial p}$. Taking the p space as one of constant curvature (radius b) I have shown⁸ that a number of facts concerning the elementary particles can be related to one another in a rational fashion

⁶ Heitler and Bhabha, *Proc Roy Soc, London*, (A), 1936, 159, 432

⁷ This fact was communicated to me in a letter from Dr W Heitler whom I have to thank for this interesting remark

⁸ M Born, *Proc Roy Soc, London*, (A), 1938, 165, 291; 166, 552

I wish to corroborate these results by a formal but rather impressive argument

If ϕ is a scalar function of space time x^k ($k = 1, 2, 3, 4$) then $\frac{\partial \phi}{\partial x^k}$ is a covariant vector. But if ϕ_k are the components of a covariant vector, $\frac{\partial \phi_k}{\partial x^l}$ is not a tensor, one has to form the covariant derivative⁹

$$(4) \quad \phi_{k;l} = \frac{\partial \phi_k}{\partial x^l} - \Gamma_{kl}^m \phi_m$$

which is a covariant tensor of the second rank. The Γ_{kl}^m are the coefficients of affine connection, symmetrical in the lower indices, they can also be defined with the help of the process of parallel displacement of a vector.

We combine this conception of relativity with the operator method of quantum mechanics. We introduce the symbol

$$(5) \quad \xi_k = \frac{1}{i} \frac{\partial}{\partial x^k}$$

which, in usual quantum theory, is the momentum operator if the units are chosen so that $\hbar = 1$. We have the identity

$$(6) \quad [\xi_k, x^l] = i (\xi_k x^l - x^l \xi_k) = \delta_k^l$$

The formula (4) shows that for particles belonging to a vectorial wave function, ξ_k cannot be considered as representing momentum since $\xi_k \phi_l$ is not a covariant tensor. We have to form the operator

$$(7) \quad p_{k;l}^m = \xi_k \delta_l^m - \Gamma_{kl}^m,$$

then $p_{k;l}^m \phi_m$ is a tensor. The quantities (7) can be considered as the mixed components $\overset{m}{p}_k$ of a tensor operator which can be abbreviated as p_k , the four p_k ($k = 1, 2, 3, 4$) form a vector, namely the momentum of the particle having a vector wave function. The product of two momentum components is defined by

$$(8) \quad (p_k p_l)^m = p_{k\alpha}^m p_{l\alpha}^m$$

The p_k do not commute among themselves, one finds for the commutator

$$(9) \quad [p_k, p_l]^m = p_{k\alpha}^m p_{l\alpha}^m - p_{l\alpha}^m p_{k\alpha}^m = P_{kl}^m,$$

where

$$(10) \quad P_{kl}^m = (\Gamma_{ln}^m \xi_k - \xi_k \Gamma_{ln}^m) - (\Gamma_{kn}^m \xi_l - \xi_l \Gamma_{kn}^m) + \Gamma_k^m \Gamma_{ln}^n - \Gamma_l^m \Gamma_{kn}^n$$

If one uses here the definition (5) of ξ_k , one can write this

$$(11) \quad P_{kl}^m = i \left(\frac{\partial \Gamma_{ln}^m}{\partial x^k} - \frac{\partial \Gamma_{kn}^m}{\partial x^l} \right) + \Gamma_{k\alpha}^m \Gamma_{ln}^\alpha - \Gamma_{l\alpha}^m \Gamma_{kn}^\alpha$$

which is (to the factor i in the first term) the definition of the curvature

⁹ We use Einstein's summation rule. If a suffix appears twice, once in an upper, once in a lower position, one has to sum over it.

tensor of 4th rank But if we understand by ξ_k the tensor $\xi_k \delta_n^m$ we can write (10) shortly

$$(12) \quad P_{kl} = i \{ [\xi_k, \Gamma_l] - [\xi_l, \Gamma_k] - [\Gamma_k, \Gamma_l] \}$$

This derivation of the curvature by commuting the process of covariant differentiation (or parallel displacement) is, of course, well known I only wish to stress the point that there may be a quantum mechanical interpretation of it which leads to a generalisation of the accepted theories In any case, (9) shows that for particles with vectorial wave functions the commutability of the components of momentum (which is generally assumed to hold) is not evident at all, but depends on the euclidicity of space

Exactly the same holds for spinor wave functions The general invariant theory of spinors has been developed by Infeld and van der Waarden¹⁰ and by Ruse,¹¹ and it is not difficult to apply similar considerations to it But I shall not go into it here as the formalism needs some lengthy explanations On the other hand, I have to stress the point that we know for certain that the wave functions of electrons and proton-neutrons have the spinor character, we are, therefore, compelled to give up the commutability of the (covariant) momenta and to introduce the notion of curvature in the quantum formalism

I shall now consider the matter from the standpoint of reciprocity If we start from the commutation law (6) connecting the ξ_k and x^l we can satisfy it not only by $\xi_k = \frac{1}{i} \frac{\partial}{\partial x^k}$ [as we did above, equation (5)], but just as well by $x_k = -\frac{1}{i} \frac{\partial}{\partial \xi^k}$ Then we are operating in the ξ -space The postulate of reciprocity says that there must be a domain of physics where point transformations in the ξ -space are permitted which induce linear transformations of the x^k (just as in the usual relativity theory the x -space can be subject to arbitrary point transformations which induce linear transformations in the p -space) Then we would have to form operators analogous to (7), namely

$$(13) \quad q_m^{k i} = x^k \delta_m^i - \Delta_m^{k i}$$

for which $q_m^{k i} \phi^m$ is a tensor in the ξ -space, being the result of covariant differentiation of $\phi^i(\xi)$ with respect to ξ_k From the standpoint of the x -space the q^k are 'covariant co-ordinates', or 'multiplication' operators

¹⁰ L. Infeld and B. L. van der Waarden, *Sitzungsber. d. Preuss. Akad. d. Wiss. Phys.-math. Kl.*, 1933, p. 380

¹¹ H. S. Ruse, *Proc. Roy. Soc. Edinburgh*, 1937, 57, 97

Then one can form the commutators of the q^k analogously to (9)

$$(14) \quad [q^k, q^l] = Q^{kl}$$

where Q_{mn}^{kl} are curvature components in the p -space, constructed from the χ^k and Δ^l in a way corresponding to (13). Finally one can commute the p_k and q^l and find

$$(15) \quad [p_k, q^l] = R_k^l$$

where the R_{km}^{ln} are mixed quantities depending simultaneously on the ξ_k , Γ_j and τ^k , Δ^l

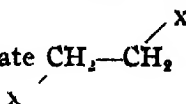
The R_k^l have, of course, to reduce to $\hbar\delta_k^l$ for the limiting case of the usual theory

If we now remark that $\hbar = ab$ where a is an absolute length and b an absolute momentum, we see that our considerations open the possibility of introducing not only the product $ab = \hbar$ in the theory, but a and b separately. For the quantity Γ_{ki}^m in (7) has evidently the dimension $a^{-1} = \hbar b$, and Δ_m^{kl} in (13) has the dimension a . Any covariant commutation rules for operators applied to vector or spinor wave functions will therefore contain the two constants a or b (or one of them and \hbar). These commutation laws may also be interpreted, as we have seen, as laws determining the curvature of space (x -space or p -space). I shall not make any attempt here to formulate these laws, as we have hardly any experimental knowledge about the domain of physics where modifications of the accepted laws must be expected. I only wish to stress the point that if it is possible to describe sub-atomic phenomena in geometrical terms the curvature equation should contain solely the constants a and b (or a and \hbar) but not the gravitational constant, as gravitation is evidently a macroscopic effect of large accumulations of neutral matter.

RAMAN SPECTRA AND MOLECULAR CONFIGURATIONS OF SOLID ETHYLENE DIHALIDES.

BY SAN-ICHIRO MIZUSHIMA AND YONEZO MORINO

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THE conspicuous difference between the Raman spectra of ethylene dihalides in the liquid and solid states was explained by us as due to the considerable change of intramolecular configuration upon solidification^{1, 2}. Below the freezing point, the molecules are almost all in the *trans*-state $\text{CH}_2\text{—CH}_2$ 

(Symmetry C_{2h}), while in the liquid state or in solutions the mean internal state shows a considerable deviation from this stable position

As the problem is concerned with one of the fundamental principles of stereochemistry, *i.e.*, the principle of free rotation around a carbon single bond, we carried out more detailed studies on the Raman spectra of these substances, the result of which will be given in the present paper

Experimental

A spectrograph of high luminosity was constructed with three 60° prisms (7 cm × 13 cm) and two achromatic lenses (diameter = 8 cm, focal length = 40 cm). This gave a dispersion of 10 Å per mm at 4000 Å. As filters, we used aqueous solution of sodium nitrite and dilute and concentrated solutions of iodine in carbon tetrachloride. The Raman tube was kept immersed in petroleum ether cooled by liquid air or by carbon dioxide and contained in a transparent Dewar vessel. The readings of temperature were made with two thermojunctions, one of them being placed in the Raman tube and the other just outside.

The results of our measurements are shown in the following tables, in which there is listed for each observed line first, its frequency in cm^{-1} , second in parenthesis, its intensity as obtained by visual estimation, third, the mercury lines exciting it. The letter *b* following the number indicating the intensity signifies a broad line and *v* in the columns of the solid spectra means the disappearance of the corresponding liquid line undoubtedly established in the accuracy of the present experiment.

¹ Mizushima, Morino and Noziri, *Sci. Papers, Inst. Phys. Chem. Research (Tokyo)*, 1936, **29**, 83 and 188.

² Mizushima, Morino and Kubo, *Physik Z.*, 1937, **38**, 459.

TABLE I

Raman Spectra of C₂H₄Cl₂

Solid (<i>ca</i> — 140° C)	Solid (<i>ca</i> — 40° C)	Liquid
53 (4) k ±	66 (4 b) k ±	
74 (6) k ±	v	125 (5 b) e ±, k ±
v	v	265 (5) e ±, k, i
303 (5) e, k	302 (5) e, k	300 (8) e ±, k, i
v	v	411 (5) e ±, k, i
v	v	654 (8) e ±, k, i, f
v	v	677 (6 b) e ±, k, i
748 (10) e, k, i, f, g	750 (10) e, k, i, f	754 (10 b) e ±, k, i
v	v	881 (4) e, k
v	v	943 (5) e, [k]
990 (3) e, k	992 (3) e, k	989 (2) e, k
1058 (2) e, k	1059 (3) e, k	1031 (2) e, k
v	v	1052 (4) e, k
		1145 (3) e, k
		1207 (5) e, k
1264 (2) e, k	1265 (2 b) e, k	1264 (3) e, k
1298 (3) e, k }	1301 (5 b) e, k	1304 (6) e, k
1312 (1) e, k }	v	1393 (1) e, k
		1429 (6) e, k
1437 (2) e, k }	1448 (2 b) e, k	1445 (4 b) e, k
1456 (2) e, k }		2844 (3) e, k
2870 (2) k	2874 (3) e, k, i	2874 (4) e, k
2965 (10) e, k, i, q, p, o	2964 (10) e, k, i	2957 (10) e, k, i
3012 (6) e, k, q	3005 (6) e, k, i	3005 (8 b) e, k, i

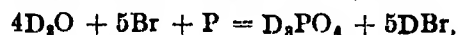
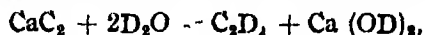
TABLE II
Raman Spectra of $C_2H_4Br_2$

Solid state (ca 40° C)	Solid state (0° C)	Liquid state
41 (4) k ± 53 (3) k ±	49 (3b) k ±	
v	v	91 (2b) e ±, k ± 132 (2) e
187 (7) e ±, k +	190 (7) e, k +	190 (10) e +, k ±
v	v	231 (3) e
v	v	325 (1) e 355 (5) e, k 469 (1) e, k
v	v	551 (8) e ±, k, i, f
v	v	583 (6 b) e ±, k, i
656 (10) e, k, i, f, g	657 (10) e, k, i, f	660 (10 b) e ±, k, i 836 (2) e 899 (3) e, k
933 (0) k	934 (1) k	933 (2) e, k 997 (0) e 1019 (1) e, k
1057 (5) e, k, i	1056 (5) e, k	1053 (9) e, k, i
1157 (1) e		1169 (3) e, k
1254 (8) e, k, i	1250 (8 b) e, k	1255 (10 b) e, k
v	v	1276 (3) e, k
v	b	1419 (3) e, k
1436 (3) [e], k	1438 (3) [e], k	1440 (5) e, k
2848 (2) e, k	2857 (3) e, k	2859 (4) e, k
v	v	2953 (8) e, k, i
2968 (8) e, k, i	2966 (10) e, k, i	2972 (10) e, k, i
3020 (2) e, [k]	3013 (5) e, k, i	3013 (4 b) e, [k]

The disappearance of some of the liquid lines in the solid spectrum, which was the most important result of our previous experiment, acquired further confirmation by the more accurate measurement of the present experiment *e g.*, in the solid spectrum (see Plate VIII) we could observe distinctly the Raman lines excited by Hg-f and Hg-g, which correspond to the symmetric C X vibrations³ (748 cm^{-1} for $\text{C}_2\text{H}_4\text{Cl}_2$ and 656 cm^{-1} for $\text{C}_2\text{H}_4\text{Br}_2$), but cou'd find no trace of strong liquid lines to be found in their vicinity even by Hg-e excitation (654 cm^{-1} for $\text{C}_2\text{H}_4\text{Cl}_2$ and 551 cm^{-1} for $\text{C}_2\text{H}_4\text{Br}_2$)

In the region of the unmodified line there were observed fairly intense Raman lines both as Stokes and as anti-Stokes which are characteristic of the solid spectra (see Tables I and II) These low frequency lines show quite different behaviours between the spectra observed at two different temperatures, one above the transition point and the other below it (A thermal transition of $\text{C}_2\text{H}_4\text{Cl}_2$ was found by us⁴ at -65°C and that of $\text{C}_2\text{H}_4\text{Br}_2$ by White and Morgan⁵ at -24°C) For each of the two ethylene dihalides we obtained only one diffuse line at higher temperature, while two sharp and fairly intense lines appeared at lower temperature⁶ (see Plate IX) As to the other Raman lines of the solid spectra we found no appreciable change on passing through the transition point except small frequency shifts observed for some lines (see Table IV)

We studied also the isotopic effect on the Raman lines of ethylene dibromide Using 99.6 per cent D_2O , we prepared heavy ethylene dibromide $\text{B}_1\text{D}_2\text{C}-\text{CD}_2\text{Br}$ according to the three following reactions



The third reaction was effected by passing the reactants over mercuric bromide on asbestos maintained at 120°C . The sample thus obtained was purified by redistillation We prepared $\text{C}_2\text{H}_4\text{Br}_2$ also in the same way

³ Mizushima and Morino, *Sci. Papers, Inst. Phys. Chem. Research (Tokyo)*, 1934, 26, 1

⁴ To be published shortly

⁵ White and Morgan, *J. Chem. Phys.*, 1937, 5, 655

⁶ Sirkar and Gupta (*Ind. J. Phys.*, 1938, 12, 35) have recently observed only one line of the frequency of 60 cm^{-1} for solid ethylene dichloride at the temperature of liquid oxygen. If there is no transition point between this temperature and -140°C , this line would correspond to the unresolved doublet of the frequencies 53 cm^{-1} and 74 cm^{-1}

⁷ Wibaut, *Rec. trav. chim.*, 1931, 50, 313

in order to prove by the observation of Raman spectrum that the reaction product consists almost entirely of ethylene dibromide contaminated with a small amount of ethylidene bromide. Thus we can safely treat the isotopic shifts of the strong lines corresponding to the totally symmetric vibrations of the *trans*-configuration (see Table III)

Discussion

As is well known the ordinary stereochemical formula for an organic molecule does not specify the molecular configuration with regard to the internal rotation around a C—C single bond, and it was for some time supposed that such an intramolecular rotation was completely free. The experimental results of dipole measurements^{8, 9, 10, 11, 12, 13} and X-ray scattering,¹⁴ however, showed that all the intramolecular rotational states are not equally probable, the most stable position corresponding to the *trans*-state with the symmetry of C_{2h} . According to the result of our intensity measurement¹³ carried out together with dipole measurement, the intensity ratio $I(\nu_1)/I(\nu_2)$ of the two strong lines ν_1 and ν_2 ($\nu_1 = 654 \text{ cm}^{-1}$ and $\nu_2 = 754 \text{ cm}^{-1}$ for $C_2H_4Cl_2$, $\nu_1 = 551 \text{ cm}^{-1}$ and $\nu_2 = 660 \text{ cm}^{-1}$ for $C_2H_4Br_2$) decreases as the mean intramolecular state approaches to the *trans*-position. Now that ν_1 disappeared completely in the solid spectrum, we expect that practically all the molecules in the solid state assume the *trans*-configuration (It is evident from Tables I and II that the thermal transitions have nothing to do with the molecular configuration). That such is actually the case was shown by our calculation³ of chain frequencies, i.e., the normal frequencies of $X-CH_2-CH_2-X$ as four-body system. The three low frequency lines observed in the solid state ($302, 750$ and 1059 cm^{-1} for $C_2H_4Cl_2$ and $190, 657$, and 1056 cm^{-1} for $C_2H_4Br_2$) are thus assigned to the normal vibrations of the chain with respect to the centre of symmetry. Taking into account the motions of hydrogen atom, one of us¹⁵ has recently calculated all the eighteen normal frequencies of the molecule of ethylene dihalide and showed that the high frequency lines observed in the solid spectrum correspond also to the normal vibrations symmetric with respect to the centre of symmetry.

⁸ Meyer, *Z. Phys. Chem.*, 1930, **B 8**, 27

⁹ Smyth, Dornte and Wilson, *J. Am. Chem. Soc.*, 1931, **53**, 4242

¹⁰ Zahn, *Phys. Rev.*, 1931, **38**, 521

¹¹ Greene and Williams, *ibid.*, 1932, **43**, 119

¹² Mizushima and Higasi, *Proc. Imp. Acad., Tokyo*, 1932, **8**, 482

¹³ Mizushima, Morino and Higasi, *Physik. Z.*, 1934, **35**, 905, *Sci. Papers, Inst. Phys. Chem. Research (Tokyo)*, 1934, **25**, 159

¹⁴ Ehrhardt, *Physik. Z.*, 1932, **33**, 605

¹⁵ Morino, *Bull. Chem. Soc., Japan*, 1938, **13**, 189.

As a further confirmation of our conclusion, we studied the isotopic shifts of the Raman lines of ethylene dibromide corresponding to the totally symmetric vibrations of the *trans*-form (Symmetry C_{2h}). The assignment of such lines was made from our calculation of normal vibrations and from the spectral features (see Table III)

TABLE III

Raman Lines of BrH_2C-CH_2Br and BrD_2C-CD_2Br Corresponding to the Totally Symmetric Vibrations of the Trans-Configuration

$C_2H_4Br_2$		$C_2D_4Br_2$	
Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
190	9	188	6
660	10	606	10
1053	4	906	2
1255	6	990	7
1440	2 b	1153	3 b
2972	5	2182	4

It was shown by Redlich¹⁶ and Teller¹⁷ that for the vibrations of the same symmetry class the ratio of the frequency products of two isotopically related molecules can be calculated with no knowledge of the force system, nor indeed of any factor except the geometry of the molecule and masses involved. Their equation applied to the present case becomes

$$\frac{\pi \nu_H}{\pi \nu_D} = \sqrt{\left(\frac{\bar{M}_D}{\bar{M}_H}\right)^3 \frac{I_H}{I_D}}$$

where M_H and M_D denote respectively, the atomic masses of hydrogen and deuterium and I_H and I_D the moments of inertia of $C_2H_4Br_2$ and $C_2D_4Br_2$ molecules about the symmetry axis C_{2h} . The evaluation of the left-hand side with the experimental values in Table III gives 2.76 and that of the right-hand side with the molecular constants, $C-H = C-D = 1.08 \text{ \AA}$, $C-Br = 1.93 \text{ \AA}$, $C-C = 1.55 \text{ \AA}$, and valency angle $= 109^\circ 28'$, gives 2.82

¹⁶ Redlich, *Z. Phys. Chem.*, 1935, B 28, 371

¹⁷ Quoted by Ingold and co-workers, *Nature*, 1935, 135, 1033.

The agreement between these two values is satisfactory, which not only justifies the above assignment but also affords another confirmation of our conclusion that the molecule of solid ethylene dihalide is nearly in a pure *trans*-state

Let us now discuss the Raman lines observed in the vicinity of the unmodified line. According to our calculation none of the normal vibrations of the ethylene dihalide molecules can have such a low frequency except the intramolecular rotatory oscillation, which is antisymmetric with respect to the centre of symmetry of the *trans*-form and is forbidden in the solid spectrum. It is, therefore, very probable that these low frequency lines correspond to some motions of a molecule as a whole in the crystal lattice,, e g , lattice vibration, and the observed change of the behaviour of these lines is caused at the transition point (-65° for $C_2H_4Cl_2$ and -24° for $C_2H_4Br_2$)

It is generally believed that many thermal transitions are caused by the setting-in of molecular rotation in the crystal lattice, for which Pauling¹⁸ first gave a theoretical treatment. The transitions of ethylene dihalides cannot, however, correspond to the onset of three-dimensional molecular rotation in the crystal lattice, as can easily be seen from the following discussion. We have already stated that below the freezing point practically all the molecules of ethylene dihalides assume the *trans*-form and the thermal transitions have no effect on this molecular configuration. This must be explained in terms of crystal forces. Such a specific effect of these forces in fixing the shape of a molecule should not be expected, if it were rotating about three axes. Taking into account our former result in Raman measurement, White and Morgan⁵ explained the thermal transition of ethylene dibromide observed by them as due to the onset of molecular rotation about only one axis, i e , that of the zigzag Br—C—C—Br chain. Rotation about this axis does not contradict the existence of the said crystal forces which keep the molecule of the solid in a nearly pure *trans*-state and it would not require a large amount of energy which is consistent with the small value of heat of transition estimated by White and Morgan. The thermal transition of ethylene dichloride can be treated quite similarly, the heat of transition estimated in our measurement⁴ being also very small as compared with the heat of fusion. The commencement of such a molecular rotation necessarily causes a change in the molecular field in the crystal lattice which affects the value of force constant and consequently the frequency of normal vibration. The small frequency shifts observed for some of the lines of solid ethylene dihalides (Table IV) might be interpreted as due to such a change in the molecular field on passing through the transition point. That we found no appreciable change in frequency for these lines on fusion would then be of particular

¹⁸ Pauling, *Phys. Rev.*, 1930, **36**, 430, see also Smyth, *Chem. Rev.*, 1936, **19**, 329.

interest when we consider that the molecules are rotating in the liquid state as well as in the solid state above the transition point

TABLE IV

Frequency Changes in Some of the High Frequency Lines of Ethylene Dihalides

$C_2H_4Cl_2$			$C_2H_4Br_2$		
Solid		Liquid	Solid		Liquid
$ca - 140^\circ C$	$ca - 40^\circ C$		$ca - 40^\circ C$	$ca - 0^\circ C$	
2870	2870	2874	2848	2857	2859
3012	3005	3004	3020	3013	3013

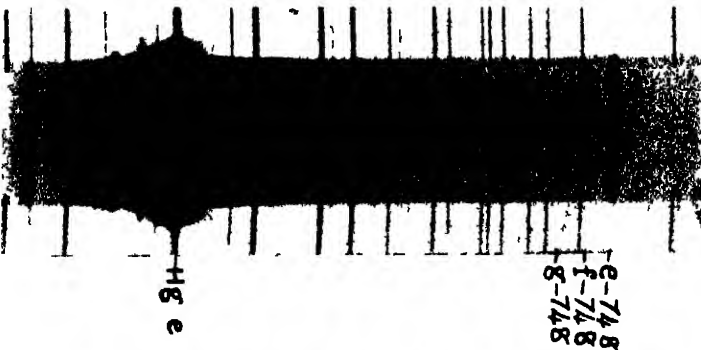
The measurement of Raman spectra at intermediate temperatures is in progress in order to confirm that the change of low frequency lines is caused at the transition point observed in the thermal measurement

We thank Prof M Katayama for his kind advice. Our thanks are also due to Nippon Gakujutsu-Shinkokai and Hattori Hokokai for grants in aid of this research

Summary

The disappearance of many Raman lines of ethylene dihalides on solidification, which was the most important result of our previous experiment, acquired further confirmation by the more accurate measurement of the present experiment. It was shown by the calculation of normal vibrations as well as by the study of isotopic effect that practically all the molecules of solid ethylene dihalides assume the *trans*-form. If, therefore, the thermal transitions observed for these solids ($-65^\circ C$ for $C_2H_4Cl_2$ and $-24^\circ C$ for $C_2H_4Br_2$) are caused by the onset of molecular rotation, this must take place about only one axis, i.e., that of the zigzag X-C-C-X chain. Such a rotation in one dimension does not contradict the existence of the crystal forces which keep the molecule of the solid in a nearly pure *trans*-state and is consistent with the small values of heat of transition estimated in thermal measurements.

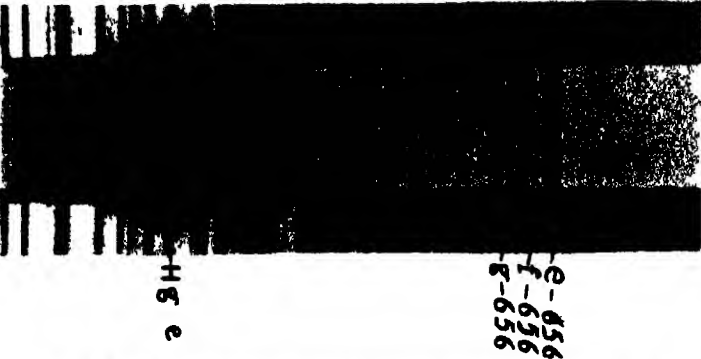
The disappearance of liquid lines in solid spectra



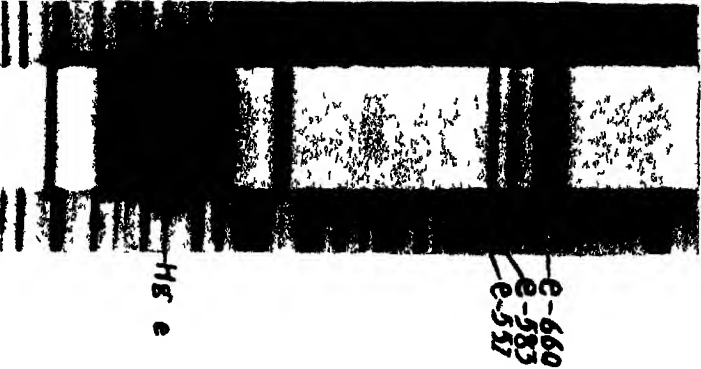
Ethylene dichloride
(solid)



Ethylene dichloride
(liquid)

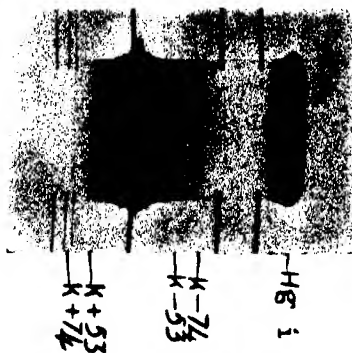


Ethylene dibromide
(solid)

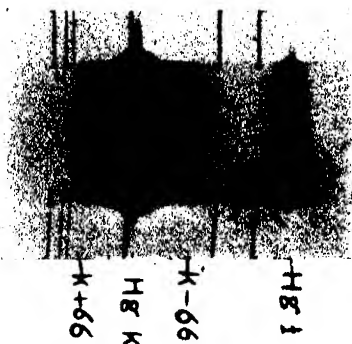


Ethylene dibromide
(liquid)

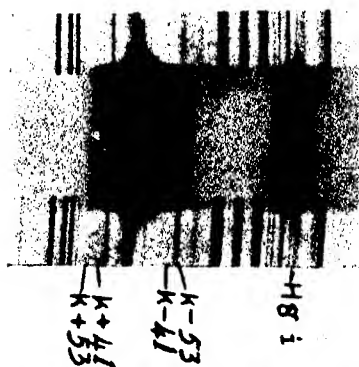
Raman Lines of solid ethylene dihalides in the region of the unmodified line.



Ethylene dichloride at ca. -140° C.



Ethylene dichloride at ca. -40° C.



Ethylene dibromide at ca. -40° C.



Ethylene dibromide at 0° C.

STUDIEN ZUM RAMAN-EFFEKT.

Mitteilung XC. Parasubstituiertes Acetophenon.

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(Mit 2 Figuren im Text)

VON den Spektren der in Para-Stellung substituierten Acetophenone $X \cdot C_6H_4 \cdot CO \cdot CH_3$ ist, soweit wir wissen, bisher nur das des Oxy-acetophenons mit $X = OH$ beobachtet worden. Im folgenden teilen wir die Resultate mit, die an den Derivaten mit $X = NH_2, OH, OCH_3, CH_3, Cl, Br$ erhalten wurden. Im I. Teil werden die Messungs-Ergebnisse zusammengestellt, im zweiten Teil folgt eine kurze Diskussion.

I Messungs-Ergebnisse

Zu den Raman-Aufnahmen wurden für flüssige oder geschmolzene Substanzen die seit vielen Jahren hier im Betrieb stehende "Normal-Apparatur", für kristall-Pulver die beiden a a O beschriebenen¹ "Festkörper-Apparaturen" F_1 ("Reflexions-Methode", Erregung durch Hg e) und F_2 (Gerlach's Methode der komplementären Filter in Ananthakrishnan's Ausführung, Erregung durch Hg k) verwendet. Bei den folgenden Angaben bedeutet t = Expositionszeit in Stunden, mF = mit Chinosol-Filter (Unterdrückung des Erregerlichtes mit $\lambda < 4358$), mFC = mit Natriumnitrit-Filter zur Unterdrückung von $\lambda < 4047$, oF = ohne Filter, ν = Aufnahmetemperatur, n = Zahl der Streulinien, aus denen das Raman-Spektrum abgeleitet wurde. In letzterem sind neben der Angabe für die Frequenz in cm^{-1} zuerst in Klammern die relative (geschätzte) Linien-Intensität, dann in der zweiten Klammer jene Hg-Linien, angeführt die als Erregerfrequenz wirkten, fehlt diesbezüglich eine Angabe, dann kam nur Hg e als Erregerlinie vor.

(1) *p-Amino-acetophenon* $H_2N \cdot C_6H_4 \cdot CO \cdot CH_3$ (Fraenkel-Landau) — Zweimalige Sublimation bei 0,01 mm Druck und Luftbad-Temperatur $120-140^\circ$, Fp 106.2° (Lit 106°). Bisherige Beobachtung: Keine Aufnahme an der in H_2 eingeschmolzenen Substanz. Pl Nr 2734, mF , $t = 8$, $\nu = 114^\circ$, Verfärbung nach tiefem Gelb. Aufnahme am Kristallpulver Pl F_1 363 bzw F_1 364, $t = 8$ bzw 24. Der Frequenzbereich unter 450 wurde nicht erfasst, einerseits wegen Gelbfärbung, andererseits wegen Ueberdeckung.

¹ Vergl etwa L. Kahovec, K. W. F. Kohlrusch, A. W. Reitz, J. Wagner, *Z. physikal. Chem.*, 1938, **39**, 481.

$\Delta \nu$ -- 482 (2), 568 (2), 633 (1), 692 (2), 824 (3), 846 (6), 893 (00), 961 (4), 1069 (8), 1173 (7), 1275 (6), 1301 ($\frac{1}{2}$), 1448 (0), 1512 (0) (e ?), 1563 (7), 1591 (10b), 1645 (5)

(2) *p-Oxy-acetophenon* $\text{HO C}_6\text{H}_4 \text{ CO CH}_3$ (Fraenkel-Landau) Zweimalige Destillation im vakuum (0,005 mm 150–160° Luftbad-Temperatur) I'p 110–111° (Lit 109°) Bisherige Beobachtung *Bonino-Manzoni-Rolla*² Aufnahme am Kristallpulver F_1 367, $t = 24$, F_2 103 und 104, $t = 24$ und 48 Aufnahme an der neuerlich zweimal destillierten und in H_2 -Atmosphäre eingeschmolzenen Substanz, die sich bei Belichtung m F stark nach gelb verfärbt Pl 2750, m F $t = 10$, $\nu = 128^\circ$

$\Delta \nu = 232$ (0) (e), 282 (0) (e), 348 (00) (e), 427 ($\frac{1}{2}$) (e), 486 (1b) (k, e) 572 ($\frac{1}{2}$ b) (e), 636 (3b) (k, e), 688 (2) (k, e), 840 (5) (k, 1, e), 960 (4) (k, f, c), 1074 (7b) (k, f, e), 1117 ($\frac{1}{2}$) (k, e), 1164 (6) (k, 1, e), 1218 (3b) (k, e), 1272 (7) (k, e), 1372 (00) (e), 1435 ($\frac{1}{2}$) (k, e), 1512 ($\frac{1}{2}$) (k, e), 1575 (8) (k, e), 1600 (8) (k, e), 1655 (7b) (e), 2923 ($\frac{1}{2}$) (k), 3070 (2) (k), 3300 (2b) (k) —

Bezüglich der Hauptlinien gute Uebereinstimmung mit den Angaben der italienischen Autoren

(3) *p-Methoxy-acetophenon* $\text{H}_3\text{C O} \cdot \text{C}_6\text{H}_4 \text{ CO CH}_3$ (Fraenkel-Landau) Zweimalige Destillation im Hochvakuum (0,005 mm 110–120° Luftbad-Temperatur) I'p 39° (Lit 39°) In H_2 -Atmosphäre eingeschmolzen Bisherige Beobachtung Keine Aufnahme an der geschmolzenen Substanz Pl 2542 und 2543, m F, $t = 6$ und 8, $\nu = 48^\circ$, Ugd m, Sp st, Pl 2544, m F C, $t = 7$, $\nu = 48^\circ$, rasche Verfärbung nach gelb, Ugd s s st, $n = 68$

$\Delta \nu = 175$ (1) (e), 278 (3) (\pm e), 297 (3) (k, e), 339 (1) (e), 507 (1) (\pm c, c), 580 (2) (\pm e, c), 628 (4) (k, \pm e, c), 679 (2) (k, \pm e), 726 (2) (k, \pm c), 804 (8) (k, \pm e, c), 833 (1) (e), 957 (5) (k, f, e), 1005 (2) (k, e), 1078 (10) (k, \pm e, c), 1171 (8) (k, 1, f, \pm e), 1252 (8) (k, 1, e), 1268 (8) (e), 1310 (4) (k, e), 1356 ($\frac{1}{2}$) (k, e), 1415 (2) (e), 1450 (1) (k, e), 1507 (1) (e), 1577 (4) (e), 1599 (15) (k, f, e), 1670 ± 7 (12b) (e), 2840 (0) (e), 2873 (3) (e ?), 2933 (3) (e), 2964 (00) (e), 3013 (1) (e), 3072 (3) (e), 3195 (0) (e ?) —

(4) *p-Methyl-acetophenon* $\text{H}_3\text{C C}_6\text{H}_4 \text{ CO CH}_3$ (Fraenkel-Landau) —Dreimalige Vakuum-Destillation Kp_{11} 97 5–98° Lit kp_{12} 94° Bisherige Beobachtung Keine Pl 2545, m F, $t = 8$, Ugd s, Sp sst, Pl 2549, m F C, Sp 0,04, $t = 7$, Ugs sst, Sp st, Verfärbung nach gelb $n = 59$

$\Delta \nu = 268$ (4b) (k, \pm e), 346 (2) (e, c), 462 ($\frac{1}{2}$) (e), 577 ($\frac{1}{2}$) (e), 633 (4) (k, e, c), 670 (1) (e), 711 (1) (e), 803 (5) (k, 1, f, e, c), 814 (2) (k, e), 956 (2) (k, e), 1071 (6) (k, f, e), 1121 (0) (k, e), 1182 (4) (k, e), 1210 (4) (k, e), 1266

² (i) B. Bonino, R. Manzoni-Anselmi, M. Rolla, *La Ricerca Scient.*, VIII/2, Nr. 5/6.

(5) (k,e), (1310) ($\frac{1}{2}$) (k, e), 1380 (3) (k,e), 1435 (1) (k, e), 1504 (3) (k, e), 1606 (15) (k,e), 1677 ± 8 (10b) (e), 2838 (2) (k²), 2918 (6) (q,p,k,e), 2974 (1) (k, e), 3009 (1) (e), 3067 (4) k, e) —

(5) p-Chlor-acetophenon $\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_3$ (Fraenkel-Landau)-Dreimalige Vakuum-Destillation $\text{Kp}_{14} 113^\circ$, $\text{Kp}_{760} 232^\circ$ (Lit 232°) Bisherige Beobachtung Keine Pl 2722, m F, Sp 0,06, $t = 8$ (uberexponiert), Pl 2723 und 2724, m F, Sp 0,04, $t = 7$ und 3,5, Pl 2725, m F C, Sp 0,04, $t = 2$, 5, Verfärbung $n = 56$

$\Delta \nu = 258$ (4b) (k, 1, 1 e), 308 (3) (k, f, \pm e, c), 397 (00) (e), 446 (00) (), 523 (1) (e, c), 580 (1) (e), 628 (5) (k, 1, f, c, c), 665 (1) (e), 764 (8) (k, g, f, \pm e, c), 956 (5) (k, 1, g, f, e), 1071 (8) (k, f, e), 1093 (5) (k, 1, e), 1176 (1) (k, 1,e), 1261 (7) (k, f, e), 1400 (1b) (k,e), (1422 (0) (e²), 1486 (1b) (e), 1589 (10b) (k, f, e), $1684 \pm 12\frac{1}{2}$ (10b) (e), 2924 (3) (k, e), 3072 (6) (k,e)

(6) p-Brom-acetophenon $\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_3$ (Fraenkel-Landau) Zweimalige Destillation im Hochvakuum (0,015 mm 100-110° Temperatur des Luft-bader), $\text{Fp} 50^\circ$ (Lit $\text{Fp} 54^\circ$) Bisherige Beobachtung Keine Aufnahme an der in H_2 Atmosphäre in das Raman rohr eingeschmolzenen Substanz die sich bei Belichtung o f rasch ziegelrot färbt Pl Nr 2706, m F, $t = 8$, Pl 2707, m F C, $t = 3$, $\nu = 64^\circ$, $n = 29$

$\Delta \nu = 148$ ($\frac{1}{2}$) (e), 158 ($\frac{1}{2}$) (e), 345 (6) (c), 434 (00) (e), 497 (0) (e), 579 ($\frac{1}{2}$) (e), 626 (3) (e), 708 ($\frac{1}{2}$ b) (e), 748 (5) (e), 815 (00) (e), 958 (2) (e), 1068 (8) (k, f, e), 1105 ($\frac{1}{2}$) (e), 1176 (4) (k, e), 1262 (4) (k, e), 1352 (0) (e), 1397 ($\frac{1}{2}$) (e), 1484 ($\frac{1}{2}$) (e), 1584 (7b) (k, f, e), 1685 (7b) (f, e), 2920 (1) e) —

II Diskussion der Ergebnisse

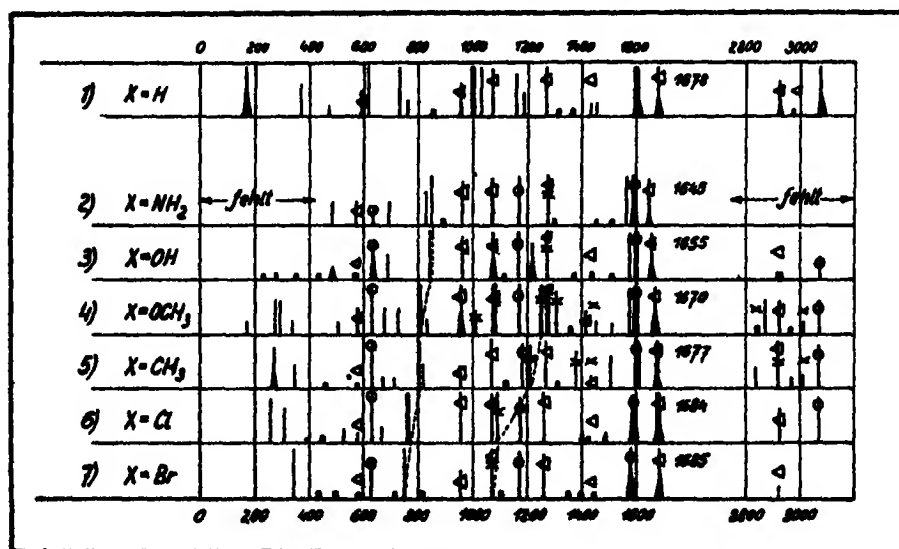


FIG. 1.

Die Ramanspektren der para-substituierten Acetophenone $\text{X} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_3$

(A) Zunächst lässt sich nach den für die Spektren von Para-Derivaten $X C_6H_4 Y$ abgeleiteten *empirischen Regeln*³ eine bereits recht weitgehende Erwartung für die Frequenz Verteilung in den Spektren der Fig 1 ableiten Und zwar

(a) Lagenkonstante und von den Substituenten X und Y fast *unabhängige* Frequenzen sollten sich bei $\Delta \nu \sim 630, 1170, 1590, 3070$ einstellen Gefunden wurde für $Y = CO CH_3$ und

X	NH ₂	633 (1)	1173 (7)	1591 (10b)	fehl
	OH	636 (3b)	1164 (6)	1600 (8)	3070 (2)
	OCH ₃	628 (4)	1171 (8)	1599 (15)	3072 (3)
	CH ₃	631 (4)	1182 (4)	1606 (15)	3067 (4)
	Cl	628 (a)	1176 (4)	1589 (10b)	3072 (6)
	Br	626 (3)	1176 (4)	1584 (7b)	fehlt

Die zugehörigen Linien wurden in Fig 1 durch Ringelung 0 gekennzeichnet

(b) In allen Para Derivaten mit konstantem Y und *variiertem* X sind für die Bindung CX charakteristische Frequenzen zu erwarten deren Werte aus den Spektren von $X C_6H_5$ zu entnehmen sind, und zwar

für	X	NH ₂	OH	OCH ₃	CH ₃	Cl	Br	J
erwartet	$\Delta \nu \sim$	1270	1253	1244	1209	1079	1068	1055

In Fig 1 gefunden $\Delta \nu -$ 1275 (6) 1272 (7*) 1252 (8) 1210 (4) 1093 (5) 1068 (8)

Sie werden bei *Kohlrausch* mit "e" bezeichnet und sind in Fig 1 ebenso wie die zu einem komplexen Substituenten X gehörigen "Inneren Gruppen-Frequenzen" durch einen Stern kenntlich gemacht Innere Frequenzen sind

für NH₂ zwei (nicht beobachtete) ν (NH)-Frequenzen um 3350

für OH eine ν (OH)-Frequenz bei 3,300

für⁴ OCH₃ eine zur Schwingung $O \longleftrightarrow (CH)$ gehörige Linie bei 1005 (2) und die

CH-Frequenzen bei 1310 (4), 1450 (1), 2840 (0), 3013 (1)

für⁵ CH₃ die CH-Frequenzen 1380 (3), 1450 (fehlt hier), 2728 (fehlt), 2862 (fehlt), 2918 (6), 3009 (1)

(c) Alle para-Derivate mit dem Substituenten $Y = CO CH_3$ müssen weiters gewisse einerseits für die Bindung $C-(CO CH_3)$, andererseits für die

³ Vergl K W F Kohlrausch *Physikal Z*, 1936, 37, 58

⁴ Vergl A W Reitz, G Prinz Ypsilanti, *Monatshefte f Chem*, 1935, 66, 299

⁵ Vergl K W F Kohlrausch, A Pongratz, *ibid*, 1934, 65, 6

inneren Schwingungen der Gruppe CO CH_3 charakteristische Frequenzen aufweisen, die (ebenso wie im vorhergehenden, den Substituenten X behandelnden Abschnitt) aus dem Spektrum des nicht substituierten Acetophenon's (Nr 1 in Fig 1) etwa durch Vergleich mit den Spektren von Benzaldehyd, Benzoesäure, Benzoesäure-Ester, Benzoylchlorid abgeleitet werden können. Es sind dies die mit Δ gekennzeichneten Linien mit den Frequenzen

		δ (CH)	ω (C=O)	ν (H)					
X = H	$\Delta \nu \sim$	590 (2)	970 (3b)	1073 (6)	1265 (7)	1428 (1)	1678 (12b)	2922 (1b)	2970 (00)
X = NH ₂		568 (2)	901 (4)	1069 (8)	1275 (9)		1645 (3)		fehlt
X = OH		572 ($\frac{1}{2}$)	900 (4)	1074 (7b)	1272 (7)	1415 ($\frac{1}{2}$)	1655 (7b)	2923 ($\frac{1}{2}$)	
X = OCH ₃		590 (2)	957 (5)	1078 (10)	1268 (8)	1415 (2)	1670 (12b)	2923 (3)	2964 (00)
X = CH ₃		577 ($\frac{1}{2}$)	956 (2)	1071 (6)	1266 (5)	1435 (1)	1677 (10b)	2918 (6)	2974 (1)
X = Cl		580 (1)	956 (5)	1071 (8)	1261 (7)	1422 (0)	1681 (10b)	2924 (3)	
X = Br		579 ($\frac{1}{2}$)	958 (2)	1068 (8)	1262 (1)		1685 (7b)	2920 (1)	

(d) Endlich ist die bei *Kohlrausch* mit "d" bezeichnete Linie zu erwarten, deren Frequenzwert von X und Y abhängig ist, das heisst sie variiert mit variablem X, wobei die Stärke des X-Einflusses sowie die Absolutwerte der Frequenzen noch von Y abhängen. Sie liegt stets zwischen 600 und 900 cm^{-1} und entspricht den in diesem Frequenzgebiet durch Punktierung mit einander verbundenen Linien der Fig 1.

(e) Sieht man von dem weniger gut bekannten Frequenzgebiet unter 550 cm^{-1} ab, so kann man also mit Hilfe dieser empirischen Regeln das Spektrum von $\text{X C}_6\text{H}_4 \cdot \text{CO CH}_3$ fast zur Gänze und fast quantitativ vorher-sagen, wenn das Spektrum von $\text{H C}_6\text{H}_4 \cdot \text{CO CH}_3$ bekannt ist.

(B) Weniger leicht und gesichert -insbesondere bei Fehlen systematischer Polarisations- und Ultrarot-Messungen- ist die Zuordnung der Frequenzen zu den Schwingungsformen von para $\text{X C}_6\text{H}_4 \cdot \text{Y}$. Ausgangspunkt für die folgenden Ueberlegungen ist die aus Figur 1 herauszulesende Tatsache, daß zwei in einem symmetrisch [mit $\text{X} = \text{Y}$] substituierten Paraderivat zwar *verbotene*, im unsymmetrisch [mit $\text{X} \neq \text{Y}$] substituierten Paraderivat *erlaubte Linien* in den Spektren 2 bis 7 der Fig 1 *fehlen*, nämlich die Frequenzen $\Delta \nu \sim 1000$ und 1025, die z. B. im Monoderivat Nr 1 kraftig auftreten. Linien mit den gleichen Frequenzwerten sollten, wie eine hier nicht wiedergegebene nähere Betrachtung des spektralen Ueberganges $\text{C}_6\text{H}_5 \rightarrow \text{X C}_6\text{H}_4 \cdot \text{Y}$ zeigt, auch in *p*- $\text{X C}_6\text{H}_4 \cdot \text{Y}$ vorhanden sein. Daß sie es nicht sind, beweist, daß die durch die Verschiedenheit $\text{X} \neq \text{Y}$ hereinge-tragene Unsymmetrie die Auswahlregeln mindestens für solche Schwingungs-formen nicht ändert, deren Frequenzen von X und Y wenig oder gar nicht

abhängen. Dieser Umstand ermutigt zu dem Versuch, als schwingendes Modell das wesentlich einfachere des symmetrischen para-Derivates $X-C_6H_4-X$ zu Grunde zu legen. Die schematisierten ebenen Schwingungsformen der Kette desselben sind in Fig. 2 zusammen mit den Auswahlregeln wiedergegeben.

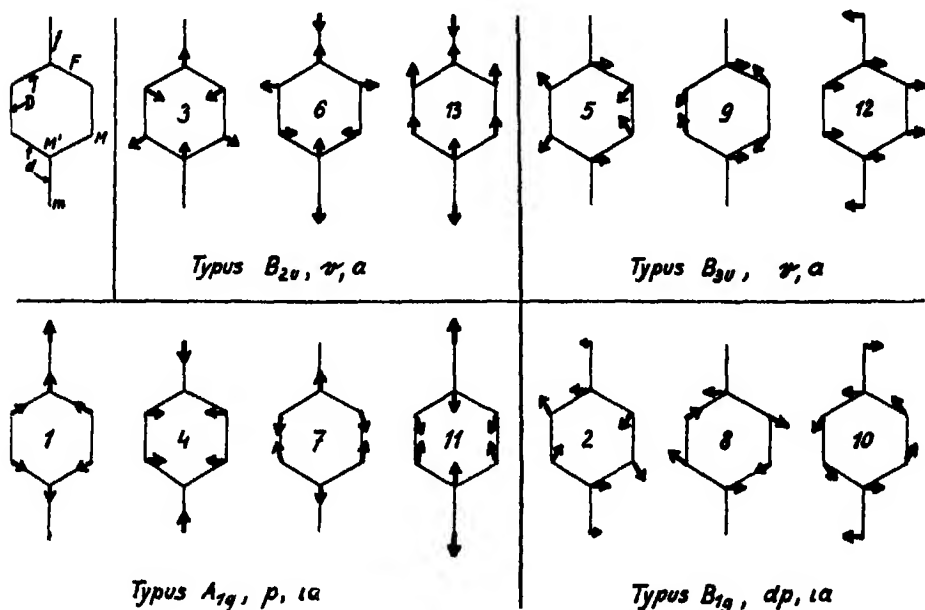


FIG. 2

Schematisierte Formen der ebenen Ketten-Schwingungen von para $X-C_6H_4-X$

Gelten die Auswahlregeln der Figur 2 im wesentlichen auch für $X \neq Y$, dann hat man sich zunächst nur um die erlaubten Schwingungstypen A_{1g} und B_{1g} der unteren Zeile zu kümmern. Die oben erwarteten, aber nicht beobachteten Frequenzen sind zugehörig zu $\omega_a \sim 1000$, das auch nach der Modellrechnung⁶ und dem Modellversuch lagenkonstant ist, sowie zu $\delta(CH) \sim 1025$, das ist einer Deformations-Schwingung der aromatischen Methingruppe.

Wir glauben folgende Zuordnung treffen zu können.

Frequenzgruppe (a) $630 = \omega_2$, $1170 = \delta(CH)$, $1590 = \omega_f$ bzw. ω_a ,
 $3070 = \nu(CH)$

Frequenzgruppe (b) soweit sie nicht "innere Schwingungen" betreffen
 Name "c" $= \omega_{11}$

⁶ Vergl. F. Trenkler, *Physikal. Ztschr.*, 1930, **37**, 338

Frequenzgruppe (c) soweit sie nicht "innere Schwingungen" betreffen
 $1265 = \omega_4$

(Hier wird das Verbot wegen Mitschwingens von X und Y aufgehoben
 Frequenzgruppe (d) Linie "d" = ω_4

Für die Zuordnung der im tiefen Frequenzbereich zu erwartenden
 Deformations Frequenzen ω_1 und ω_{10} finden wir keine Anhaltspunkte

(C) Schließlich mochten wir auf folgendes verweisen Die CO-Frequenzen
 im Amino-und Oxy-acetophenon liegen merklich tiefer als in allen andern
 Fällen, solche Abweichungen werden gerne⁷ als Assoziations-Anomalien
 gedeutet Der Vergleich der Spektren von Fig 1 und die oben durchge-
 führte, für sie alle einheitliche Analyse zeigt nun, daß es *nur* die CO-und
 wahrscheinlich noch die OH-und NH₂-Frequenzen sind, die auf Assoziation
 deutlich ansprechen Das restliche Spektrum ist durchaus normal

⁷ Vergl. z.B. L. Kahovec, K. W. F. Kohlrausch, *Z physikal. Chem*, 1937, B 88, 119.

STUDIEN ZUM RAMAN-EFFEKT.

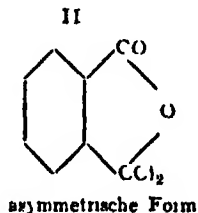
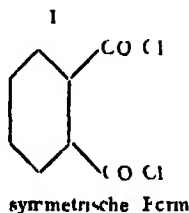
Mitteilung XCI Asymmetrisches Phthalyl-Chlorid.

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(Mit 1 Figur im Text)

Im Ramanspektrum des Phthalsäure-chlorides I wurden¹ drei CO-Frequenzen gefunden, und zwar 1736 (5), 1788 (5), 1844 (2). In Analogie zum Befund an Phthalsäure-Dimethylester wurde vermutet, daß die höchste Frequenz $\Delta\nu = 1844$ zur asymmetrischen Molekülform II gehöre, Kahovec-Kohlrausch² interpretierten weiter $\Delta\nu = 1788$ als zur Normalform I gehorig, während $\Delta\nu = 1736$ von der CO-Gruppe dimerer, durch Assoziation (Ausbildung von Wasserstoff-Brücken) entstandener Moleküle stammen solle.



In der zuletzt genannten Arbeit wurde auch über einen vorläufigen Versuch berichtet, das Spektrum der asymmetrischen Form durch Aufnahme der geschmolzenen Substanz zu gewinnen. Doch findet bei hoher Temperatur eine teilweise Rückbildung zur symmetrischen Form statt, so daß man wieder nur an einem Gemisch I + II beobachtet, in dem allerdings Form II beträchtlich angereichert sein sollte. Es ergaben sich dabei für die CO-Frequenzen die folgenden Werte und Intensitäten:

1736 (3), 1791 (4), 1845 (3),

so daß in Übereinstimmung mit der ursprünglichen Vermutung eine Intensitäts-Verschiebung zu Gunsten der zu II gehorigen Frequenz 1845 festzustellen war. Es stand also zu erwarten, daß die homogene Substanz II nur die letztere CO-Frequenz aufweisen werde. Diese Erwartung erfüllte sich nicht!

¹ K. W. F. Kohlrausch, A. Pongratz, W. Stockmair, *Monatshefte f. Chem.*, 1935, 67, 104.

² I. Kahovec, K. W. F. Kohlrausch, *Ztschr. physikal. Chem.*, 1937, 38, 119.

Das zur eben erwähnten Schmelzaufnahme verwendete Präparat war aus symmetrischem Phthalylchlorid durch Erhitzen mit AlCl_3 hergestellt worden, Nach dem Zersetzen des Reaktionsproduktes mit heiss wurde mit Petroläther ausgeschüttelt, im Hochvakuum destilliert (0,02 mm, 100–110° Temperatur des Luftbades), und in H_2 -Atmosphäre in das Ramanrohr geschmolzen. Dieses selbe Präparat wurde für die im Folgenden zu besprechenden Aufnahmen am Kristall-Pulver mit Petroläther digeriert, abgesaugt, mit Petroläther nachgewaschen und so wie früher zweimal im Hochvakuum destilliert. Fp 85° (Lit 89°). Aufnahme am Kristallpulver in der Festkörper-Apparatur F_1 auf Pl 353 bzw 354 mit $t = 24$ bzw 48^h, der Frequenzbereich $\Delta\nu < 500 \text{ cm}^{-1}$ wird bei diesen Aufnahmen nicht erfasst. Das Versuchsergebnis wird im folgenden zuerst zahlenmäßig, dann in Fig 1 zeichnerisch dem an symmetrischem (I) und an geschmolzenen unsymmetrischen (I + II) Phthalylchlorid erhaltenen Befund gegenübergestellt.

I flüss	157 (10)	215 (5)	252 (2)	268 (2)	324 (2)	350 (2)	404 (6)
I + II geschm	148 (2)	188 (½)	242 (½)				402 (2) 452 (1½)
II krist	←	verdeckt					→
I flüss	504 (10)	638 (4)	660 (8)				858 (½) 895 (½)
I + II geschm	525 (½)	550 (1b) 642 (1b)		714 (0)			816 (½) 903 (0)
II krist	536 (2)	583 (1)	640 (3)	677 (1)	713 (1)	735 (3)	781 (1) 832 (1) 910 (1b)
I flüss	1013 (2)	1047 (8)		1166 (4)	1202 (10)	1331 (½)	
I + II geschm	1003 (2)	1040 (3)	1067 (1)	1165 (1)	1205 (3)		1396 (00)
II krist	1007 (6)	1042 (0)	1105 (3)	1165 (2)	1203 (½?)		1359 (½) 1405 (00)
I flüss	1469 (2)	1589 (10)	1736 (5)		1787 (5)	1844 (2)	3080 (2)
I + II geschm	1476 (0)	1589 (5b) 1736 (3b)			1791 (4b)	1845 (3b)	3091 (0)
II krist	1471 (1)	1598 (6)		1762 (3)	1797 (3–4)	1814 (6)	3076 (3b)

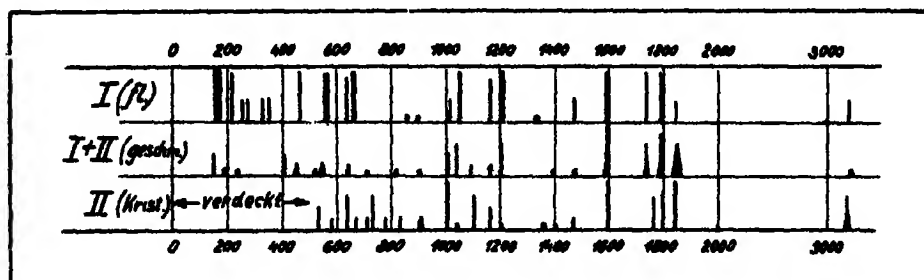


FIG 1

Die Ramanspektren von symmetrischem (I), geschmolzenem asymmetrischen (I + II) und kristallisiertem (II) Phthalylchlorid

Ohne derzeit auf die Einzelheiten dieser Spektren näher einzugehen, sei nur kurz vermerkt. Das Kristallpulver II zeigte Spuren von Feuchtigkeit

und vorzeitiges Weichwerden beim Schmelzen, man konnte also noch Beimischung von I vermuten. Der spektrale Befund besagt jedoch, daß es sich dabei nur um ganz geringe Mengen von I handeln kann, denn von den in Spektrum I auftretenden starken Linien $\Delta\nu$ 564 (10), 660 (8), 1047 (8), 1202 (10) sind in Spektrum II nur mehr Spuren vorhanden. Keinesfalls kann die Beimischung von I groß genug sein, um für das neuerliche Auftreten von drei kraftigen CO-Frequenzen in Spektrum II irgendwie verantwortlich gemacht werden zu können. Die Sache liegt also so, daß zwar die Besonderheiten des Spektrums I durch die Annahme einer Beimischung von Substanz II erklärt werden können, daß aber die Besonderheiten von Spektrum II *nicht* auf eine Beimischung von Substanz I zurückgeführt werden können.

Die Verhältnisse beim sogenannten asymmetrischen Phthalylchlorid liegen also nicht so einfach, wie erwartet wurde. Im Frequenzbereich 500 bis 1700 cm^{-1} , in dem—handelt es sich doch sowohl bei I als bei II um ortho-substituiertes Benzol—spektrale Ähnlichkeit bestehen sollte, ist der Typus der Spektren von I und II überraschend verschieden. Im Frequenzgebiet um 1800 dagegen, in welchem man zufolge des verschiedenartigen Einbaues der CO-Gruppe in den Strukturen von I und II deutliche spektrale Unterschiede erwarten sollte, findet man überraschende Ähnlichkeit.

Zu einer näheren Diskussion dieser Verhältnisse ist das Erfahrungsmaterial zu dürftig. Es besteht daher die Absicht die Erfahrungs-Grundlagen zu erweitern durch Beobachtung einerseits an substituierten Phthalylchloriden, bei denen die asymmetrische Form meist die stabilere ist, andererseits an den asymmetrischen Phthalsaureestern.

THE RAMAN SPECTRA OF VOLATILE FLUORIDES. APPLICATIONS OF RAMAN SPECTRA TO CHEMICAL PROBLEMS.

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California Institute of Technology No 672.)

Introduction

THE results and theory of Raman spectra are of importance to chemists in that the spectra yield, (1) information that is useful in establishing the structure of molecules, (2) quantitative data on vibrational and, occasionally, rotational energy states of molecules, and (3) information that permits the evaluation of the strengths of chemical bonds

The application to the determination of molecular structure (shape) depends on the effect of molecular symmetry on the number of Raman lines permitted by the selection rules¹ This application is limited in that a permitted line may not be observed, if the electrons are so bound that the tensor components of electric polarizability of the molecule are very small for the mode of vibration corresponding to the line in question, then the intensity of the line may be so small that it is not observable It is also possible for harmonics and overtones to appear in Raman spectra, and these are sometimes a source of confusion in molecular structure studies

The vibrational energy states furnished by Raman spectra are of considerable importance in both pure and applied chemistry By their use it is often possible to evaluate heat capacities, free energies and entropies of chemical compounds The limitations of this application depend on the fact that the Raman spectrum of a molecule does not always give all of the vibrational energy states Also, the degeneracies of the levels may be in doubt If, in addition to the Raman spectrum, light polarization experiments are made and the infra-red absorption spectrum determined, then one is often in a position to evaluate correctly and completely the vibrational energy states and their degeneracies A complete knowledge of these states alone suffices for the calculation of the heat capacities at room temperatures and above, of all but a few molecules in the gaseous state, since at these temperatures the rotational energy states are completely excited When it is difficult to photograph the Raman spectrum (e g, in case the substance is highly coloured), or if frequencies are forbidden or too weak to be observed in

both the scattered and infra-red spectrum, gas heat capacity measurements may be employed to determine the unknown vibrational energy states. Neither the Raman nor the infra-red spectra yield interatomic distances for molecules with large moments of inertia, and in such cases it is necessary to obtain this information from the results of electron diffraction experiments. A complete thermodynamic calculation requires that both the vibrational and rotational energy states be known, and the latter are calculable from the moments of inertia of the molecule. The refinements necessary to take account of the anharmonicity of the vibrational states, and the interaction between rotation and vibration are, in many cases, unimportant in the estimation of thermodynamic quantities.

The determination of bond force constants from spectroscopic data cannot be said to be in a completely satisfactory state, since, for reasons of mathematical simplicity, the potential functions employed are restricted to homogeneous quadratic forms. Moreover, even a homogeneous quadratic potential function which takes into account all interactions often contains more independent force constants than can be evaluated from the experimental data. In such cases one must neglect some constants on the assumption that they are small, or attempt to combine properly the data for two or more molecules containing the same bonds. In spite of these limitations the force constants that have been calculated are of significance in that they permit of a reasonably definite quantitative statement regarding the strengths, for small displacements, of chemical bonds. These bond strengths are often in accord with the qualitative notions gained from studies of stabilities and heats of formation of compounds.

*Raman Spectra of Volatile Fluorides and their Comparison
with Chlorides and Bromides*

Fluorides in general are either quite volatile or quite involatile. To obtain the spectra of the former in the liquid state requires, therefore, a low temperature technique. Again, some fluorides attack glass unless care is exercised to avoid moisture and this, in addition to the general requirements of purity (often not emphasized), renders necessary more than the usual precautions in preparing the compounds studied.

Attempts have been made at this laboratory to photograph the Raman spectrum of liquid fluorine³ at liquid air temperatures but without success. Either fluorine does not scatter strongly (from Hg 5461 Å) or the Raman line coincides with a mercury line. An estimate of the frequency has been made from the F-F distance³ of 1.46 Å as determined in this case from rather difficult electron diffraction experiments and Badger's⁴ rule. The F-F distance seems too large as will be indicated below, the calculated frequency is

$\omega = 836 \text{ cm}^{-1}$ A directly determined value of ω is highly desirable both for an understanding of the emission spectrum⁵ of F_2 and for the better estimation of the F-F distance and the entropy (48.6 cal/deg at 25°)

The boron halide molecules, BX_3 , are known to be planar with the X-atoms at the corners of an equilateral triangle and the boron atom at the centre⁶. The selection rules permit only three of the four distinct fundamentals in the Raman effect, but due to the fact that boron is light and exists as the two isotopes B^{10} and B^{11} some of the Raman lines appear doubled, namely those for which the boron atom moves appreciably, ω_2 and ω_3 . It also happens that the harmonic of the forbidden fundamental ω_3 is permitted and appears with BCl_3 and BBr_3 . Table I contains the frequencies,⁷ the B-X stretching force constants K, the bending force constants G and the B-X distances⁸.

TABLE I
Raman Frequencies and Force Constants for Boron Halides
 ω in cm^{-1} Parentheses adjoining ω contain degeneracies

	$\omega_1 (1)$	$\omega_2 (1)$	$\omega_3 (2)$	$\omega_4 (2)$	$K \times 10^{-5}$ dyne/cm	$G \times 10^{-5}$ dyne/cm	$B - \lambda$ $A = 10^{-8} \text{ cm}$
BF_3	883	722 694	1448 1501	430-513	6.69	0.88	1.30
BCl_3	471	902 (943)	940 989	253	3.30	0.43	1.73
BBr_3	279	743 (780)	806 840	151	2.50	0.27	1.87

The force constants K show that the B-F bond is, for small displacements, about twice as strong as the B-Cl bond, and this in turn is 1.3 times as strong as the B-Br bond. As will be seen below these same ratios are found for other halides. Interactions between stretching and between bending forces have been assumed in arriving at the formulæ for evaluating K and G, but for the sake of simplicity the interaction constants are not given in the table. ω_1 refers to the symmetrical swelling vibration and ω_2 to that in which the B atom moves perpendicular to the plane of the F atoms. Of the two values given for ω_2 and ω_3 , the upper refers to B^{10}X_3 and the lower to B^{11}X_3 .

The fifth group trihalides have been investigated both with respect to the Raman frequencies and the polarization of the scattered radiation⁹. The

molecules have a regular pyramidal structure,¹⁰ four Raman lines are permitted and four are observed. Table II contains the Raman frequencies together with the stretching and bending force constants K and H respectively as calculated by Howard and Wilson.¹¹ The spectra, polarization measurements, and electron diffraction results provide sufficient data for the calculation of the entropies S°_{298} of four of the MX_3 halides. These and some free energies, ΔF°_{298} , are included in the table.

TABLE II
*Raman Spectra, Force Constants and Entropies of Some
Fifth Group Trihalides*
 ω in cm^{-1}

	$\omega_1(1)$	$\omega_2(1)$	$\omega_3(2)$	$\omega_4(2)$	$K \times 10^5$ dyn/cm	$H \times 10^{-5}$ dyne/cm	S°_{298} cal/deg
Pb_3	890	531	840	480	4.56	1.07	61.2
PbCl_3	510	257	480	190	2.11	0.31	74.7
PBr_3	380	162	400	116	1.02	0.27	
AsF_3	707	341	644	274	3.90	0.40	69.2
AsCl_3	410	193	370	159	2.01	0.23	78.2

$\text{P}(s) + 3/2 \text{Cl}_2(g) \rightarrow \text{PCl}_3(g),$	$\Delta F^\circ_{298} = -62,220 \text{ cal}$
$\text{As}(s) + 3/2 \text{F}_2(g) \rightarrow \text{AsF}_3(g),$	$\Delta F^\circ_{298} = -189,000 \text{ cal}$
$\text{As}(s) + 3/2 \text{Cl}_2(g) \rightarrow \text{AsCl}_3(g),$	$\Delta F^\circ_{298} = -62,075 \text{ cal}$

Noteworthy in the case of these halides is the fact that the M-F bond force constants are about twice those of the corresponding M-Cl constants that is $K_{\text{MF}}/K_{\text{MCl}} = 2.16$ for phosphorus halides and 1.95 for the arsenic halides. The ratio $K_{\text{MCl}}/K_{\text{MBr}} = 1.3$. These ratios are closely the same as those given above for the corresponding boron halides, namely 2.0 and 1.3 respectively. It is of interest to examine this ratio for other compounds of P, Cl and Br. For the simple compounds HF, HCl and HBr one finds that $K_{\text{Hl}}/K_{\text{HCl}} = 1.8$ and $K_{\text{HCl}}/K_{\text{HBr}} = 1.3$, that is the bonds formed by these three halides have nearly the same relative strengths as those in the boron and fifth group halides. On proceeding to the molecules F_2 , Cl_2 and Br_2 one finds $K_{\text{Cl}_2}/K_{\text{Br}_2} = 1.3$ but, using $\omega = 836 \text{ cm}^{-1}$, $K_{\text{F}_2}/K_{\text{Cl}_2} = 1.15$, this latter ratio suggests that the 836 cm^{-1} calculated from $\text{F}-\text{F} = 1.46 \text{ \AA}$ and Badger's rule is not the correct value. If one assumes that ω is about the same as that found for an excited state⁸ of F_2 , namely, 1070 cm^{-1} , then $K_{\text{F}_2}/K_{\text{Cl}_2} = 1.9$, a value nearly equal to those found for other sets of halide compounds. This suggests again, but does not prove, that $\omega = 836 \text{ cm}^{-1}$ and hence $\text{F}-\text{F} = 1.46 \text{ \AA}$ are not the correct values for these constants.

The tetrahalides of the fourth group elements, with the exception of the fluorides, have been extensively investigated with respect to the frequencies and polarization of Raman scattered radiation.¹⁰ The following Table III contains the data of other investigators for the chlorides and that from this laboratory for the fluorides.¹² The results for SiF_4 are new and were obtained by Messrs Best and Trampe at this laboratory. The compound proved difficult to prepare pure, and the two weaker lines of the Raman spectrum were obtained only after rather long exposures. For CF_4 the ω_3 frequency comes from the infra-red spectrum.¹³ The tetrachlorides yield all of the Raman lines permitted by the selection rules and sometimes overtones and accidental ones (Fermi degeneracy) as well. The accepted assignment of frequencies is borne out by polarization measurements and normal co-ordinate treatments.¹ The frequency ω_3 does not appear with the tetrafluorides, although it is not forbidden. The fluorides resemble the hydrides, CH_4 , SiH_4 , in that their scattering power for some fundamental modes is not so great as that of the chlorides. Molecules containing light atoms frequently do not scatter as well as those containing heavy atoms.

TABLE III
Raman Frequencies, M - X Force Constants and
Entropies of Four Tetrahalides

ω in cm^{-1}

	ω_1 (1)	ω_2 (2)	ω_3 (3)	ω_4 (4)	$h \times 10^5$ dyn/cm	$M - X$ Å	S°_{298} cal/deg
CF_4	904	437	1350	635	(3.5)	1.46	62.7
CCl_4	450	214	775	311	1.78	1.755	74.1
SiF_4	797	268	(1000)	463	(5)	1.54	67.0
SiCl_4	422	148	608	220	2.55	2.02	79.2

The force constants for the C-F and Si-F bonds have not been carefully calculated. The values in the table are estimates only, but are probably of the right order of magnitude. The entropies given may be used in connection with heats of formation and the entropies of the constituent elements to calculate the free energies of formation. It is of interest that low temperature heat capacity measurements yield for the standard entropy of $\text{CCl}_4(g)$ at 25° the same value,¹⁴ 74.4 cal/deg, within the limits of experimental error, as that calculated from the spectroscopic and electron diffraction data, this increases our confidence in the application of Raman spectra results to such calculations.

It is not always convenient in obtaining first notions about the assignment of Raman frequencies to the fundamental modes of vibration to resort to the use of normal co-ordinate treatments and force constants. This may sometimes be done by comparing the spectra of two analogous compounds for which the frequency assignment of one is known. Also it is sometimes possible to make a fairly reliable determination of corresponding frequencies for two analogous compounds. Best and Trampe at this laboratory have photographed recently the Raman spectrum of thionyl fluoride, SOF_2 . They used material that was fractionally distilled several times at solid carbon dioxide temperatures in the absence of moisture. Their results along with those of Masotti and Aderhold,^{2a} and Nis1^{2a} for thionyl chloride are presented in Table IV. The molecules are pyramidal in form, the oxygen and both chlorine atoms being bound to the sulphur atom which stands at the apex of the pyramid. The selection rules permit six Raman lines and six are observed. All of the frequencies are nondegenerate. The numbers in parentheses adjoining the frequency values are estimated relative intensities.

TABLE IV
The Raman Spectra of SOF_2 and SOCl_2

SOF_2	326 (1)	395 (6)	529 (8)	720 (9)	795 (9)	1312 (10) cm^{-1}
SOCl_2	192 (s)	282 (s)	343 (vs)	443 (s)	488 (s)	1229 (m) cm^{-1}

s = strong, vs = very strong, m = medium

Since SO_2 has one strong line at 1146 cm^{-1} it seems reasonable to suppose that the frequencies 1312 and 1229 correspond to a motion in which the S-O bond is stretched appreciably. The totally symmetric frequency of SF_6 (*vide infra*) is 770 cm^{-1} , accordingly, for SOF_2 , the 720 and 795 cm^{-1} frequencies are those for which the S-F bonds undergo appreciable stretching. The lowest frequencies, as is usual, probably correspond to bending motions. Now since the ratio of corresponding frequencies for fluorides and bromides (Tables I-III) varies from 1.7 to 2.0 it seems likely that 443 and 488 cm^{-1} are the frequencies of SOCl_2 that correspond to 720 and 795 cm^{-1} for SOF_2 . Again, 192 and 282 cm^{-1} must correspond to bending vibrations in SOCl_2 since they are low. The corresponding frequencies are, from these rough considerations, probably those given in the table. The application of a normal co-ordinate would establish more definitely whether or not the general modes of motion assigned to the frequencies were the correct ones. Attention must be drawn to the fact that if all bending, stretching and interaction energies are invoked in this case the potential function will contain more than six force constants. It must also be remarked that since none of the

vibrational energy levels are degenerate, a knowledge of the assignment of the frequencies to fundamental modes is quite unnecessary in order to make thermodynamic calculations

The Raman spectra of the very interesting hexafluorides of sulphur, selenium and tellurium were photographed by Yost, Steffens and Gross.¹⁵ These molecules contain the six fluorine atoms at the corners of a regular octahedron, the remaining atom being at the centre. The selection rules permit only three of the six distinct frequencies in the Raman spectrum and only three are observed. Of the remaining three frequencies only two are permitted in the infra-red. The sixth frequency, as a fundamental, is forbidden in both the Raman spectrum and the infra-red. Eucken, Bartolomé, and others have investigated the heat capacities and infra-red spectra of all three of the hexafluorides and their results taken together with the Raman spectra serve to establish quite definitely the vibrational energy states of these molecules. The normal co-ordinate treatment of this type of molecule was first made by Redlich, Kurz and Rosenfeld.¹⁶ Other more extensive treatments have since been given^{15, 17, 18} some of which involve bending as well as stretching of the bonds. The following table presents the six fundamental frequencies for each hexafluoride together with the M-F stretching force constants K given by Sachse and Bartolomé,¹⁹ and the M-F distances²⁰

TABLE V
The Vibrational Frequencies of SF_6 , SeF_6 and TeF_6

	SF_6	SeF_6	TeF_6
ω_1 (1)	775	708	701
ω_2 (2)	615	662	674
ω_3 (3)	525	405	313
ω_4 (3)	363	245	165
ω_5 (3)	617	461	370
ω_6 (3)	965	787	752
$K \times 10^{-5}$	3.44	3.68	3.95
M - F in Å	1.58	1.70	1.84

$$S^{\circ}(SF_{6g}) = 71 \text{ cal/deg} \quad S(s) + 3F_2(g) = SF_6(g) \quad \Delta F^{\circ}_{298} = -238,000 \text{ cal}$$

Of interest is the fact that K does not depend strongly on the nature of the central atom

The value of ΔF°_{298} for SF_6 can be used to show that the compound has a strong tendency to hydrolyze in water, although the rate of the reaction is

effectively zero This result is of interest in connection with possible applications of the substance

The applications of Raman spectra to chemical problems are not restricted to the comparatively simple molecules discussed above Some progress has been made toward the solution of the problem of restricted rotation about the bonds in compounds such as C_2H_6 , Si_2H_6 , Si_2Cl_6 ,²¹ CF_3CH_3 So far the Raman spectra alone have not been able to give a decisive answer to the question, but their use in connection with low temperature heat capacity measurements has served to show that for the carbon compounds at least, the rotation of MX_3 radicals about single bonds is restricted²²

From the simple considerations presented here it appears evident that the results of Raman spectra have proved extremely useful in the solution of several of the many problems that face the present-day chemist

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THE RELATION BETWEEN THE FORCE CONSTANT, THE INTER-NUCLEAR DISTANCE, AND THE DISSOCIATION ENERGY OF A DIATOMIC LINKAGE

BY G B B M SUTHERLAND

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DURING the past ten years there have been several attempts to establish an empirical relation between the force constant characterising the vibration frequency of a diatomic linkage and the inter-nuclear distance of the two atoms. In 1929 Morse¹ pointed out that the product of the vibration frequency (ω_e) into the cube of the inter-nuclear distance (R_e) was approximately constant for a considerable number of diatomic molecules.

Mathematically — $\omega_e R_e^3 \sim 3 \times 10^{-21}$ —Morse Rule. This empirical rule held best for molecules in which the masses of the two atoms were approximately equal, the numerical value of the product tending to increase for more unsymmetrical molecules. In 1934 modifications of this simple rule were suggested independently by Douglas Clark² and by Badger³ which gave better agreement over a wider distribution of molecules and molecular states. The former suggested the relation

$$\omega_e R_e^3 \sqrt{N} = K \quad \text{Clark Rule,}$$

where N is the "group number", K is a constant for a given "molecular period," if we confine our attention to un-ionised molecules. The "group number" is a number defined by Clark as the number of electrons in the molecule which are in molecular rather than atomic orbitals. The "molecular period" is defined by the positions in the periodic table to which the constituent atoms belong, e.g., the molecules BO , CN , CO all belong to the KK period. The modification suggested by Badger is expressed by the equation

$$R_e = \left(\frac{C_{11}}{K_e} \right)^{\frac{1}{2}} - D_{11} \quad \text{Badger Rule}$$

Here K_e is the force constant derived from the vibration frequency, C_{11} , and D_{11} , are constants which vary according to the molecular period. It was pointed out by Allen and Longair⁴ that the Clark Rule is theoretically weak in that it is obviously wrong for the case of isotopic molecules. They suggested a third relation which may be put in the form

$$R_e^3 = \frac{C_{11}}{(K_e)^{\frac{1}{2}}} \quad \text{Allen-Longair Rule}$$

The fact that so many variations all give reasonable agreement indicates that each is only an approximation to some more refined rule. Clark and Stoves⁵ have made a careful study of their application to 70 states of 33 non-hydride diatomic molecules from which it appears that a later modification of Clark's rule (in which K may vary according to the electronic configuration within a molecular period) is slightly superior to the others in the case of molecules of the I, II, and higher periods. For molecules containing one atom in the K period, the original Clark Rule is just as good or better than the more complicated one.

There has been little or no attempt to find a theoretical basis for any of the above relations, presumably because the evaluation of the potential function, even for the simplest diatomic molecule, viz., H_2 , involves laborious computations. Newing,⁶ using very general arguments and the methods of quantum mechanics, has been able to show that relations of the type

$$R_e = R_e(\omega_e, X_e, D_e, \mu)$$

should exist where X_e is the anharmonic constant, D the dissociation energy and μ the reduced mass, but he has been unable to produce anything more specific. On the other hand, the same author has indicated how, by using a more classical approach and assuming that the mutual potential energy has the form*

$$V = \frac{ZZ'}{R} - A - \frac{C_1}{R} - \frac{C_2}{R^2} -$$

the result

$$K_e = \frac{1}{R_e^3} \left[(ZZ' - C_1) - \frac{3C_2}{R_e} - \frac{6C_3}{R_e^2} - \dots \right]$$

may be deduced. This is really equivalent to Badger's relation

$$K_e = A (R_e - D_e)^{-3} = \frac{A}{R_e^3} \left(1 - \frac{3D_e}{R_e} - \frac{6D_e^2}{R_e^2} - \frac{10D_e^3}{R_e^3} - \dots \right).$$

We wish now to show how this approach may be generalised to lead to some very suggestive and interesting results. Let us start from the assumption that the mutual potential energy may be expressed as follows—

$$V = \frac{a}{R^m} - \frac{\beta}{R^n} \quad (1)$$

Since $\left(\frac{\partial V}{\partial R}\right)_{R=R_e} = 0$, we obtain the relation

$$ma = n\beta R_e^{m-n} \quad (2)$$

Next we expand V about R_e in ascending powers of $(R - R_e)$. The

* Here Z and Z' are the effective charges on the nuclei while A , C_1 , C_2 , etc., are constants.

coefficient of $(R - R_e)^2$, i.e., the force constant K comes out to be

$$K_e = \frac{n\beta}{R_e^{n-1}} \left\{ \frac{n+1}{R_e} - \frac{m+1}{R_e} \right\}. \quad (3)$$

Using the relation (2) this may be expressed either as

$$K_e = \frac{n\beta(n-m)}{R_e^{n+2}} \quad (4)$$

or as

$$K_e = \frac{ma(n-m)}{R_e^{m+2}} \quad (5)$$

It should be noted that if we take $n = 4$, then (4) is equivalent to the Allen-Longair relation, while if we take $M = 1$ then (5) is very similar to Badger's relation. In the latter case we should have to replace R_e by $R_e - D_{11}$, i.e., an effective internuclear distance instead of the actual. It is interesting that the Clark formula is not substantiated, and indeed it is difficult to see how it can be in any theoretical treatment, since the presence of the mass factor in using ω_e instead of K_e is insuperable. The fact that the Clark formula is slightly superior to the other two must be put down to the fact that the variable constants are more skilfully chosen to follow variations in going from one family of molecules to another. It should be remembered that in the Allen-Longair formula, only one arbitrary constant is available as against two in the Clark and Badger relations. A modification of the Allen-Longair formula involving two arbitrary constants, say, of the form

$$R_e^2 \sqrt{N} = \frac{C''}{(K_e)^{\frac{1}{2}}}$$

ought to yield more satisfactory agreement. The use of two constants could only be justified if m varied from one family of molecules to another. Similarly, a modified Badger formula of the type

$$\sqrt{N} K_e = \frac{C''}{R_e^3}$$

might yield better results, on the assumption that n rather than m varied on going from one molecular group to another. These possibilities are now being investigated.

Next we consider the dissociation energy of the linkage. This is readily seen to be

$$D = \frac{a}{R_e^m} \left\{ 1 - \frac{m}{n} \right\} \quad \text{using (2)}$$

$$= \frac{K_e R_e^2}{mn} \quad \text{using (5)}$$

This result is at once reminiscent of an empirical rule of Mecke⁷ which defined the strength of a bond as the work required to increase the nuclear

separation to twice its equilibrium value, assuming that Hooke's law of force holds. The proportionality which Mecke proposed between the energy of a bond and the product $K_e R_e^2$ on a very questionable assumption is now seen to be justified in a slightly modified form, using a much more plausible and general assumption. The present derivation is much more satisfactory also in that it is from the same assumption that the empirical relation between force constant and internuclear distance has been justified. From the above, one would expect a constant ratio between the dissociation energy and the product $K_e R_e^2$ for molecules of the same class, i.e., for which m and n will not vary appreciably. This has been found to be the case, as the following small table will illustrate.

Molecule	D in volts	$K_e R_e^2$ in arbitrary units	$\frac{D}{K_e R_e^2}$
O ₂	5.1	52	0.98
S ₂	4.45	40	1.11
SO	5.1	55	0.93
CN	6.7	70	0.96
NO	5.3	66	0.80

The full working out of this has not been completed. It obviously depends partly on a satisfactory substitute being found for the Badger or Allen-Longair relation. This would yield a definite value for the constants M , N , α and β and thus enable the three quantities K_e , R_e and D_e to be completely correlated. The application of these results to polyatomic molecules is also being investigated. The importance of the above theory in treating the results of observations on Raman spectra is quite obvious. It should enable a fairly accurate estimate to be made of the internuclear distance and of the dissociation energy of a bond in any molecule for which the force constant K_e has been determined from analyses of the Raman spectrum.

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INTERPRETATION OF RAMAN SPECTRA IN CRYSTALS: ANHYDRITE AND GYPSUM.

BY S BHAGAVANTAM

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1 Introduction

THE application of group theory to a study of the normal modes of oscillation of crystal lattices with special reference to Raman scattering has yielded very fruitful results. A comprehensive account will be published separately. The two interesting cases of anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are dealt with in the present paper. The fact that the crystal structures as well as the Raman spectra of both these substances have been studied in considerable detail is of great help in this connection.

2 Crystal Structure

The crystal lattice of anhydrite is an ionic one. The crystals belong to the orthorhombic variety and the space group is V_h^{17} . The unit cell contains four molecules. The structure of gypsum is also ionic and the unit cell which belongs to the monoclinic class contains again four molecules. The space group is C_{2h}^1 . Attempts have been made to fix the atomic positions in both these cases from the results of X-ray analysis and it is believed that the SO_4 ions preserve their tetrahedral symmetry in the crystalline state also. In the present paper, we will consider the anhydrite crystal as consisting of Ca and SO_4 groups and gypsum as consisting of $\text{Ca} \cdot 2\text{H}_2\text{O}$ and SO_4 groups. Further details in respect of these well-known structures may be obtained from Wyckoff ¹

3 Raman Spectra

The Raman spectra of anhydrite and gypsum have been studied by a number of investigators. Complete references are to be found in Landolt Bornstein Tabellen. The frequencies given below are taken from these Tables.

TABLE I Raman Frequencies

Substance	Lattice	Internal to SO_4 ion				Water bands
SO_4 ion		454 (ν_2) double	622 (ν_3) triple	983 (ν_1) single	1106 (ν_4) triple	
CaSO_4 (Anhydrite)	126 169 233 (1) (2) (1)	415 499 (1) (5d)	609 628 674 (2) (2) (8)	1018 (15)	1108 1128 1160 (2) (10) (5)	
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)		414 494 (5) (3)	618 672 (2b) (4)	1008 (20)	1113 1135 (2) (10)	3402 3491 (10d) (20)

¹ The Structure of Crystals, 2nd Edn, 1931

The case of the free SO_4 ion is also included for comparison. The frequencies have been divided into various classes, the division being self-explanatory. The degree of degeneracy and the conventional designation is indicated in each case for the frequencies of the free ion. As the corresponding modes are well known, they need not be described here in detail. The splitting in the crystalline state of all the degenerate frequencies belonging to the tetrahedral SO_4 ion is noteworthy. This result has been described by Nisi² as being inconsistent with the X-ray evidence and was taken to indicate a departure from the tetrahedral symmetry for the SO_4 ions in the crystalline state. The present investigation on the contrary, shows clearly that the splitting is to be expected since the crystal as a whole does not possess the high degree of symmetry that is characteristic of the SO_4 ion. The result is therefore not inconsistent with the view that the SO_4 ions preserve their tetrahedral symmetry in the crystalline state.

4 Symmetry Properties and Character Tables

TABLE II

Anhydrite

V_k	F	C_1	C_2	C_2'	σ_h	σ_v	σ_v'	n_i	External		n_i'	Raman	Infra red
									T	L			
A_{1g}	1	1	1	1	1	1	1	12	0	4	4	p	f
A_{2g}	1	-1	1	-1	1	-1	-1	10	0	6	4	p	f
B_{1g}	1	1	-1	1	1	-1	-1	4	0	2	2	p	f
B_{2g}	1	-1	1	1	-1	-1	1	10	0	6	4	p	f
A_{1u}	1	1	1	1	-1	-1	1	4	0	2	2	f	f
A_{2u}	1	-1	1	1	1	-1	1	10	1	5	4	f	p
B_{1u}	1	1	-1	-1	1	1	1	12	1	3	8	f	p
B_{2u}	1	1	1	1	-1	1	-1	10	1	5	4	f	p
U_r	24	8	0	0	0	0	16	16					
h, χ'	72	8	0	0	0	0	16	16					

² *Proc. Phys. Math. Soc., Japan*, 1933, 15, 463.

TABLE III

Gypsum

C_{2h}	E	C_2	σ	n_i	External		n_i'	Raman	Infra red
					T	L_z			
A_1	1	1	1	1	0	0	10	ρ	f
A_2	1	-1	-1	20	0	12	8	p	f
B_1	1	1	-1	16	1	5	10	f	p
B_2	1	-1	1	20	2	10	8	f	p
U_r	24	8	0	0					
h, χ'	72	8	0	0					

The notation is the same as that employed in earlier papers published in these *Proceedings*. n_i' represents the number of oscillations that are internal to the SO_4 group. p and f under the columns Raman and infra-red indicate respectively that the line is permitted or forbidden from appearing. We will first consider the internal oscillations n_i' . A very complete analysis of all the normal modes appropriate to the unit cell³ has been made with a view to understand the significance of the splitting in each case. The details will not be given here, but we will state the results. In each crystal there are 36 internal oscillations. The four distinct modes of oscillation appropriate to the free SO_4 group split into nine distinct modes in the crystal as the degeneracy disappears on account of its lower symmetry. These nine distinct modes undergo a further splitting on account of the fact that there are four such groups in each unit cell, thus giving an aggregate of 36 modes. The former splitting may be expected to be more prominent than the latter. Detailed analysis shows that one or other of the four components coming from each one of the nine fundamental modes falls in the Raman active class and we should accordingly expect both anhydrite and gypsum to exhibit all the nine components in their respective Raman spectra. As these components are only slight modifications of the original modes, we may further expect a close correspondence between the split frequencies in the crystal and those of the free ion. The results in respect of the internal oscillations given in Table I completely support this view. The correspondence between

³ These modes when extended to an infinite lattice will correspond to the limiting frequencies of the various optical series in the notation of Born and Karman. The pure translations given under T constitute the acoustic series.

the degenerate frequencies of the free SO_4 ion and the split components in the crystal is evident. The results in respect of gypsum suggest that one faint line in the neighbourhood of 600 and another in the neighbourhood of 1160 are yet to be recorded.

The experimental results in respect of the lattice oscillations are by no means definite. Many weak lines reported by different investigators have been omitted from Table I as their reality is somewhat uncertain. The investigations described in the present paper show that several more lattice frequencies are to be expected than those contained in Table I. In fact the figures given in Landolt but not included here show that the low frequency spectrum of gypsum is quite complex. A more complete experimental investigation of these low frequencies is obviously necessary. The water bands present a problem by themselves and will be dealt with separately.

5 *Summary and Conclusion*

Application of group theory to a study of the normal oscillations of the crystal lattices of anhydrite and gypsum shows that we should expect the degenerate modes of the free SO_4 ion to completely split up in the crystal. All the split components are Raman active. The experimental results obtained with anhydrite are in entire agreement with this view. The case of gypsum also gives results which are in general agreement with the theory. The splitting is a consequence of the lower symmetry of the crystals as a whole and need not be taken as indicating a lack of tetrahedral symmetry for the SO_4 ions individually.

NORMAL FREQUENCY OF THE DIAMOND LATTICE.

BY T VENKATARAYUDU

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1 Introduction

SEVERAL earlier attempts have been made to determine the normal modes of oscillation of the diamond lattice. In view of the great importance attached to the case of diamond, the problem has attracted the attention of many theorists as well as experimenters. Detailed references are to be found in the recent papers by Nagendra Nath¹ and Robertson, Fox and Martin². The fact that the Raman spectrum of diamond consists of only one strong line at 1332 is of the utmost significance in this connection. Other weak lines have however, been recorded, but their intensity is almost negligible. In the course of a systematic investigation of the normal oscillations of crystal lattices³ some interesting results have been obtained in the case of diamond and a brief account of these is given here. The conclusions which are identical with those of Nagendra Nath are arrived at in a much simpler and more elegant manner in the present investigation.

2 The Basis of the Diamond Lattice

It is well known that the diamond lattice may be regarded as having been made up of two interpenetrating cubic face-centered lattices. Each atom of one lattice is at the centre of the tetrahedron formed by its four nearest neighbours of the other lattice. The positions of the atoms in the lattice are usually given with reference to the edges of the unit cube as axes. Accordingly the co-ordinates of the eight atoms in the unit cube are given by $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$, $(\frac{3}{2}, \frac{1}{2}, \frac{3}{2})$, $(\frac{1}{2}, \frac{3}{2}, \frac{3}{2})$.

The above description of the structure of diamond is no doubt convenient in visualizing the lattice, but it is misleading inasmuch as it leaves the impression that the basis of the crystal is the unit cube. This however, is not the case since a translation of the whole lattice through any one of

¹ *Proc Ind. Acad Sci*, 1934, 1, 333

² *Phil Trans Roy. Soc*, (A), 1934, 232, 403

³ The details and the results in respect of various other crystals will form the subject-matter of a separate communication

$(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$ makes the lattice identical with itself. The proper basis of the diamond lattice consists of two atoms (1 and 5) only and their positions referred to rhombohedral axes (Fig. 1) are respectively $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

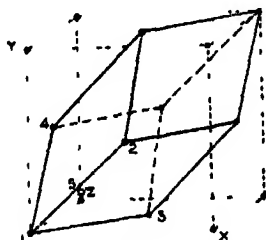


FIG. 1

3 Normal Mode and Frequency of Oscillation

The symmetry operations pertaining to the point group O_h of such a lattice are

E, 8 C_3 , 3 C_2 , 6 σ , 6 S_6 , 1, 8 S_6 , 3 σ , 6 C_3 and 6 C_2 .

The corresponding character table is given below. The notation employed is the same as that used in earlier papers in these *Proceedings*⁴.

O_h	E	$8C_3$	$3C_2$	6σ	$6S_6$	1	$8S_6$	3σ	$6C_2$	$6C_3$	n_i
A_{1g}	1	1	1	1	1	1	1	1	1	1	0
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	0
E_g	2	-1	2	0	0	2	-1	2	0	0	0
F_{1g}	3	0	-1	-1	1	3	0	-1	-1	1	0
F_{2g}	3	0	-1	1	1	3	0	-1	1	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	0
A_{2u}	1	1	1	-1	1	-1	-1	-1	1	1	0
E_u	2	-1	2	0	0	-2	2	-1	0	0	0
F_{1u}	3	0	-1	-1	1	-3	0	1	1	-1	0
F_{2u}	3	0	-1	1	-1	-3	0	1	-1	1	1
U_u	2	2	2	2	2	0	0	0	0	0	
χ_i, χ_i'	6	0	-6	12	-12	0	0	0	0	0	

⁴ *Proc Ind Acad Sci*, 1938, 3, 101

The selection rules for this group require that the lines coming under the class F_{2g} should be Raman active and infra-red inactive. The mode coming under F_{2u} is a pure translation. We thus see that the diamond lattice has only one limiting normal mode of oscillation which is Raman active and infra-red inactive. The normal co-ordinates corresponding to this triply degenerate oscillation and the translation are

$$\left. \begin{aligned} Q_a &= x_1 - x_2 \\ Q_b &= y_1 - y_2 \\ Q_c &= z_1 - z_2 \end{aligned} \right\} \quad F_{2g}$$

$$\left. \begin{aligned} Q_x &= x_1 + x_2 \\ Q_y &= y_1 + y_2 \\ Q_z &= z_1 + z_2 \end{aligned} \right\} \quad F_{2u}$$

The normal co-ordinates show that the two interpenetrating lattices are oscillating against each other, the direction of oscillation being arbitrary.

The potential energy function may be formed in terms of three types of forces, namely the primary valence, the directed valence, and the repulsive forces between the distant atoms. The co-ordinates of the atoms in the displaced positions corresponding to the normal mode Q_a are given below. The axes of co-ordinates are the edges of the unit cube and $2a$ stands for the length of the edge of the cube (Fig. 1). δ is the amplitude of oscillation.

	x	y	z
1	δ	0	0
2	$a + \delta$	a	0
3	$a + \delta$	0	a
4	δ	a	a
5	$\frac{a}{2} - \delta$	$\frac{a}{2}$	$\frac{a}{2}$

The variations in the lengths of the valence bonds and the valence angles may be obtained as

$$\Delta R_{12} = \Delta R_{45} = -\Delta R_{25} = -\Delta R_{35} = -\frac{2\delta}{\sqrt{3}}$$

$$\Delta\phi_{123} = \Delta\phi_{124} = \Delta\phi_{234} = \Delta\phi_{345} = 0 \text{ and } \Delta\phi_{134} = -\Delta\phi_{253} = \frac{8\delta}{\sqrt{6}}$$

There will be no variation in the distances between the nearest atoms belonging to the same lattice as the atoms of the same lattice move in the same direction by the same amount. If N is the total number of atoms in the lattice, the kinetic and potential energies are given by

$$2T = N m \dot{\delta}^2$$

$$2V = N \left[\frac{8}{3} K_1 + \frac{64K_2}{3 p^2} \right] \delta^2,$$

where m , p , respectively stand for the mass of a carbon atom and the length of a valence bond, K_1 and K_2 are the primary and the directed valence force constants. The frequency of oscillation is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{8}{3m} \left(1 + \frac{8K_2}{p^2} \right)}$$

This expression is identical with that obtained by Nagendra Nath except that K_2 takes the place of $K^1 - K^{111}$.

4 Summary and Conclusion

The diamond lattice has only one limiting normal mode of oscillation. In this mode the two interpenetrating lattices oscillate against each other, the direction of oscillation being arbitrary. The corresponding frequency is active in the Raman effect and inactive in infra-red absorption. The fact that we get only one Raman line possessing a very large intensity is in agreement with the above results. The weaker lines and also the infra-red absorption maxima are to be regarded as secondary effects.

I wish to thank Prof. S. Bhagavantam for his kind assistance in the preparation of this paper.

THEORETISCHE BEMERKUNGEN ZUM R. S. KRISHNAN'S REZIPROZITATSGESETZ DER KOLLOID-OPTIK.

VON V S VRKLJAN

BEKANTLICH hat unlängst R S Krishnan¹ ein Gesetz der Kolloid-optik entdeckt, das von ihm als Reziprozitätsgesetz genannt wird. Die ursprüngliche Form dieses Gesetzes war in der einfachen algebraischen Form

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v) \quad (1)$$

zusammengefasst, wo ρ_v , ρ_h und ρ_u die Depolarisationsgrade des in der horizontalen Ebene senkrecht zum einfallenden Licht beobachteten zerstreuten Lichtes bedeuten, die Indexe v und h beziehen sich dabei auf die Polarisation des einfallenden Lichtes (elektrische Schwingung vertikal bzw horizontal), während sich der Index u auf das unpolarisierte einfallende Licht bezieht. Später aber ist die Gleichung der Form

$$H_v = V_h \quad (2)$$

als der eigentliche Inhalt des Reziprozitätsgesetzes mehr und mehr in den Vordergrund getreten.² Hier bedeutet H_v die Intensität der horizontalen Komponente des zerstreuten Lichtes, wenn der elektrische Vektor des einfallenden polarisierten Lichtes vertikal ist, und V_h die Intensität der vertikalen Komponente des zerstreuten Lichtes beim horizontalen elektrischen Vektor des einfallenden polarisierten Lichtes. In der neuesten Zeit hat R S Krishnan³ hervorgehoben, dass die Gleichung (2) auch für schräge Beobachtungsrichtungen in der Horizontalebene gültig ist.

Es drängt sich damit die Frage auf, was man auf Grund der Theorien für schräge Beobachtungsrichtungen, die nicht in der Horizontalebene liegen, sagen kann. Hier wird diese Frage auf Grund der Mie'schen Theorie behandelt.*

Wir nehmen also an, dass sich die einfallende ebene polarisierte Welle durch ein Medium der Dielektrizitätskonstante ϵ_a und der spezif Leitfähigkeit $\sigma = 0$ in der entgegengesetzten Richtung der Z-Koordinate fortprop-

* Dass neue Gans'sche Theorie des Krishnan-Effektes (*Phys ZS*, 1926, 37, 19) dem Reziprozitätsgesetz (2) für senkrechte Beobachtungsrichtung in der Horizontalebene genügt, ersieht man ohne weiteres aus den Gleichungen (11) und (14) der Abhandlung von R Gans, die die quadratischen Mittelwerte der elektrischen Feldstärken f_z (falls der elektrische Vektor des einfallenden polarisierten Lichtes horizontal ist) und f_x (falls der elektrische Vektor des einfallenden polarisierten Lichtes vertikal ist) ergeben.

flanzt, stellen uns im Koordinatenursprung ein Kugelchen (im Sinne der Mie-schen Theorie) dar und stellen uns weiter die Frage auf, was für ein Gesetz, das dem Krishnan'schen Reziprozitätsgesetz entsprechen sollte, auf Grund der Mie-schen Theorie für schräge Richtungen in der schrägen Beobachtungsebene zu erwarten wäre. In diesem Falle erhält man, wie bekannt,⁴ für die ψ - und ϑ -Komponente des elektrischen Vektors des zerstreuten Lichtes ausserhalb der Wellenzone

$$E_{\psi}' = - \frac{e^{-i\mu_a r}}{l_a} \cdot \frac{\sin \psi}{r} \sum_{s=1}^{\infty} i^s \left[B_s \frac{P_{s,1}(\cos \vartheta)}{\sin \vartheta} + B_s^* \frac{d P_{s,1}(\cos \vartheta)}{d(\cos \vartheta)} \sin \vartheta \right] \quad (3)$$

$$E_{\vartheta}' = - \frac{e^{-i\mu_a r}}{l_a} \cdot \frac{\cos \psi}{r} \sum_{s=1}^{\infty} i^s \left[B_s \frac{d P_{s,1}(\cos \vartheta)}{d(\cos \vartheta)} \sin \vartheta + B_s^* \frac{P_{s,1}(\cos \vartheta)}{\sin \vartheta} \right] \quad (4)$$

falls der elektrische Vektor der primären einfallenden Welle horizontal ist. Hier bedeutet l_a die Kurzung für den Ausdruck $\frac{2\pi}{\lambda} \sqrt{\epsilon_a} =$ Wellenlänge, (π = Ludolf'sche Zahl),

r den Abstand des Aufpunktes vom Koordinatenursprung,

ψ den Winkel zwischen der horizontalen XZ-Ebene und der schiefen durch die Z-Achse gelegten Beobachtungsebene,

ϑ den Winkel zwischen dem Radius-Vektor r und der Z-Koordinatenachse, $P_{s,1}(\cos \vartheta)$ die sog. zugeordneten Kugelfunktionen,

B_s und B_s^* die Konstanten, die durch gewisse Grenzbedingungen⁵ bestimmt sind.

Im Falle aber, wo der elektrische Vektor der primären Welle (deren Intensität gleich ist wie in vorhergehendem Falle) vertikal ist, erhält man ebenso für das zerstreute Licht auf Grund der sog. Potential ausserhalb der Wellenzone

$$F_{\psi}'' = \frac{e^{-i\mu_a r}}{l_a} \cdot \frac{\cos \psi}{r} \sum_{s=1}^{\infty} i^s \left[B_s \frac{P_{s,1}(\cos \vartheta)}{\sin \vartheta} + B_s^* \frac{d P_{s,1}(\cos \vartheta)}{d(\cos \vartheta)} \sin \vartheta \right] \quad (5)$$

$$E_{\vartheta}'' = - \frac{e^{-i\mu_a r}}{l_a} \cdot \frac{\sin \psi}{r} \sum_{s=1}^{\infty} i^s \left[B_s \frac{d P_{s,1}(\cos \vartheta)}{d(\cos \vartheta)} \sin \vartheta + B_s^* \frac{P_{s,1}(\cos \vartheta)}{\sin \vartheta} \right] \quad (6)$$

Beobachten wir das zerstreute Licht in einer schrägen Beobachtungsebene und bezeichnen wir die Intensität derjenigen Komponente, deren elektrischer Vektor in der Beobachtungsebene liegt, mit P , und die Intensität derjenigen Komponente, deren elektrischer Vektor normal zur Beobachtungsebene steht, mit N , so können wir sofort ersehen, dass N , proportional

mit $|E_{\psi}''|^2$ ist, N_h proportional mit $|E_{\psi}'|^2$, P_r proportional mit $|E_{\vartheta}''|^2$ und schliesslich P_h proportional mit $|E_{\vartheta}'|^2$ ist

Aus den Gleichungen (5) und (3) einerseits und (4) und (5) andererseits kann man sofort ableiten

$$\frac{N_i}{N_h} = \frac{P_h}{P_i} = c i g^2 \eta \quad (7)$$

Nehmen wir jetzt an, dass das einfallende Licht unpolarisiert ist. Dann wird der Wert des Depolarisationsgrades für das zerstreute Licht im erweiterten Sinne der Krishnan'schen Definition

$$\rho_{ii} = \frac{P_i + P_h}{N_h + N_i} \quad (8)$$

welche Gleichung wegen der Relation (7) sofort ergibt

$$\rho_{ii} = \frac{P_i}{N_h} \quad (9)$$

Diese Gleichung für den Depolarisationsgrad des zerstreuten Lichtes bei unpolarisiertem einfallenden Lichte kann man als eine auf Grund der Mie-schen Theorie abgeleiteten Erweiterung der Krishnan'schen Relation (1) ansehen. Sie gibt uns den Depolarisationsgrad ρ_{ii} des zerstreuten Lichtes bei unpolarisiertem einfallenden Lichte in Beziehung mit den Komponenten P_r und N_h des zerstreuten Lichtes, die bei dem polarisierten einfallenden Lichte (das in beiden Fällen gleicher Intensität ist) beobachtbar sind. Die Gleichungen (8) und (9) sind auch, wie auf Grund der Ableitung sofort zu ersehen ist, für schräge Richtungen in den schragen (also nicht horizontalen¹⁾) Beobachtungsebenen gültig. Was die experimentelle Bestätigung der Gleichungen (8) und (9) betrifft, so ist diese dort zu erwarten, wo die Voraussetzungen der Mie-schen Theorie wenigstens angenähert erfüllt sind.

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EFFET RAMAN ET STRUCTURE DES COMPOSES AX^5 : PENTACHLORURE DE PHOSPHORE ET HOMOLOGUES.

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I Introduction

DE toutes les molécules simples les molécules de formule AX^5 paraissent être les moins étudiées du point de vue de leurs propriétés physiques, ce qui tient peut-être aux difficultés inhérentes à leur manipulation. Elles présentent pourtant un intérêt tout particulier car une structure moléculaire ayant une symétrie d'ordre 5, s'il en existe, pourrait donner lieu à des conclusions théoriques importantes.

C'est pourquoi nous avons entrepris une étude systématique de diverses propriétés. Spectre Raman et spectre d'absorption, chaleur spécifique, etc., de ces molécules, étude qui n'est qu'à son début mais qui permet déjà de résoudre certaines contradictions apparentes entre les résultats des auteurs antérieurs.

Nous exposerons ici surtout nos résultats concernant le spectre Raman de PCl^5 , en n'indiquant nos autres résultats qu'à titre de confirmation.

II Quelques données physicochimiques sur PCl^5

On sait que les méthodes classiques de détermination des édifices moléculaires n'ont pas permis jusqu'à maintenant de conclure à une structure définie de PCl^5 bien que les résultats expérimentaux ne soient pas contestables en eux-mêmes ¹.

Ainsi par exemple, PCl^5 réagit avec les indènes, à basse température comme une molécule de forme $PCl^4 \cdot Cl$, dans laquelle le groupement PCl^4 se fixe d'un bloc, ² tandis que la réaction avec les indones (elle n'a lieu que vers 160–180°) conduit à attribuer au PCl^5 une forme $PCl^3 \cdot Cl^2$ ⁽³⁾. De même les données anciennes sur le point de fusion diffèrent entre elles ⁴.

¹ Voir en particulier le *Congrès de Chimie Solvay* 1931, p. 304 (Gauthier-Villars, éditeur), et les mémoires de Lewis, *Valence et structure des Atomes et Molécules*, p. 105 (Braunschweig, 1927), Langmuir, *J. Am. Chem. Soc.*, 1920, 41, 919, Prideaux, *Chem. and Ind.*, 1925, 42, 672.

² Bergmann et Bondi, *Ber.*, 1930, 63, 1158.

³ W. Schlenk et E. Bergmann, *Annalen*, 1928, 463, 218; Ch. Mourou, Dufrainne, et Badoche, *Bull. Soc. Chim.*, 1928, 43, 1391.

⁴ Prideaux, *J. Chem. Soc.*, 1907, 91, 1711; Smith et Calvert, *J. Am. Chem. Soc.*, 1914, 36, 1363.

On sait encore que PCl^5 possède dans certains solvants un moment électrique de 0,9 D,⁵ et que sa constante diélectrique et sa conductibilité sont plus grandes à l'état solide qu'à l'état liquide,⁶ ce qui est assez exceptionnel pour les conducteurs non-métalliques. Les cristaux de PCl^5 appartiennent au système quadratique.⁷

III Le spectre Raman de PCl^5

Nous avons étudié⁸ le spectre Raman de PCl^5 solide, liquide, vapeur, ainsi que dissous dans PCl^3 et CCl^4 . Nos résultats sont consignés dans le Tableau I.

Dans un deuxième tableau (2) figurent les fréquences de Cl^2 , de PCl^3 et de POCl^3 , d'après les Tables Annuelles de Constantes.

TABLEAU I

PCl^5

Liquide			Solide			Vapeur	Sol CCl^4	Sol PCl^3		
$\Delta\nu \text{ cm}^{-1}$	Intensité	ρ	$\Delta\nu \text{ cm}^{-1}$		Intensité	$\Delta\nu \text{ cm}^{-1}$	$\Delta\nu \text{ cm}^{-1}$	$\Delta\nu \text{ cm}^{-1}$	Intensité	ρ
			nous	P. K. ⁹						
100	10 (l)	P				~ 90	97 ± 2	90		P
190	0, 7 (d)	6/7				226	163 ± 2	189		6/7
			244	248	4 (s)					
271	6, 3 (s)	6/7					265 ± 3	287		
			356	357	10 (s)			351	f	P
392	6, 5 (ss)	P				400	390	393	m	P
			409	405	2 (s)					
449	0, 2 (d)	6/7	450	450	8 (s)					.
495	0, 2 (d)	6/7			.					

⁵ Truncel, *C R*, 1936, 202, 37.

⁶ Simons et Jessop, *J. Am. Chem. Soc.*, 1931, 53, 1263.

⁷ P. Groth, *Chem. Kristallographie I*, p. 231 (Leipzig, 1906).

⁸ H. Moureu, M. Magat et G. Wettrich, *C R*, 1937, 205, 276.

⁹ Une colonne (P. K.) contient les données relatives à l'état solide de P. Krishnamurti (*Ind. J. Phys.*, 1930, 5, 116) que nous confirmons entièrement.

TABLEAU II

POCl ³ liquide			PCl ³ liquide			Cl ² gaz
$\Delta\nu$ cm ⁻¹	Intensité	ρ	$\Delta\nu$ cm ⁻¹	Intensité	ρ	$\Delta\nu$ cm ⁻¹
193	8	6/7	189	10 (s)	6/7	550
267	6	P	260	10 (s)	P	
337	7	6/7				
486	10	P	485	6 (d)	6/7	
			512	10 (d)	P	
581	3	6/7				
1200	5	P				

On voit qu'aucune des fréquences attribuables à PCl³ ne peut provenir de ces trois substances qui, en raison des précautions expérimentales, pourraient être à priori les seules impuretés possibles

Les données sur le spectre Raman du PCl³ gazeux effectuées à 160°, contenues dans le premier tableau, proviennent de l'étude microphotométrique d'un seul cliché. Les raies signalées, à peine perceptibles, sont indiquées sous toute réserve

Ce qui frappe surtout dans le tableau I, c'est le fait que les spectres du solide et du liquide diffèrent totalement, aussi bien en ce qui concerne les fréquences que le nombre de raies observées. Nous pouvons donc conclure que la structure de la molécule PCl³ est différente à l'état solide et à l'état liquide. Une expérience, faite au point de fusion même, montre une superposition des deux spectres. Le changement de la structure moléculaire s'effectue donc au moment de la fusion.

A l'état dissous, on retrouve le spectre de la forme liquide presque pur dans CCl⁴ et le spectre de mélange des deux formes dans PCl³. Enfin la structure à l'état gazeux paraît analogue à celle de l'état liquide.

L'existence de deux formes de PCl³ en proportion dépendant de la température et du solvant permet de comprendre la possibilité de deux modes de réaction chimique de cette molécule (voir II). D'autre part, le fait que la transformation s'effectue au point de fusion permet de d'interpréter un phénomène assez inattendu que nous avons observé et dont voici les traits essentiels.

IV La fusion du PCl^{B}

Si l'on chauffe lentement du $\text{PCl}^{\text{B}(10)}$ sous sa propre tension de vapeur dans une ampoule cellée, la substance fond "normalement" à $159-160^\circ$, 5°C ,¹¹ le palier s'étale sur 1° , 5 malgré la pureté du corps, et la température recommence à s'élever quand un tiers du produit est encore solide. Quand, après fusion totale, on laisse refroidir le corps, on s'aperçoit que le phénomène n'est pas réversible. En effet, le palier de cristallisation s'établit toujours plus bas, entre 148° et 154°C suivant la vitesse de refroidissement. Il ne s'agit pas de surfusion, car, 1° /de nombreux cristaux se forment à partir de 157° , 2° /il n'y a pas de remontée de température au moment de la cristallisation massive.

Ce phénomène ne s'explique ni par la présence d'impuretés (des distillations répétées dans une atmosphère de Cl_2 ou de N_2 ne changeant rien), ni par décomposition en PCl^{B} et Cl^{B} (¹²).

L'existence de deux formes moléculaires rend fort bien compte de nos observations. Si l'on admet en effet que le point de fusion de la forme solide est supérieur à celui de la forme ayant la structure du liquide, c'est la transformation d'une forme dans l'autre qui détermine la liquéfaction. La "surfusion" et la "surcristallisation" ne sont que des conséquences du fait que la transformation se fait avec une vitesse finie, inférieure ou au plus égale à la vitesse de cristallisation et qui est en fonction de la température.

Enfin des mesures préliminaires de l'énergie de fusion donnent une valeur de l'ordre de 10 kcal (des expériences beaucoup plus précises sont en cours). Elle est beaucoup plus grande que la chaleur de fusion de composés voisins: SbCl^{B} $1,92\text{ kcal}$, POCl^{B} $3,02\text{ kcal}$. Cette valeur anormalement élevée conduit donc aussi à penser qu'un phénomène de transformation se superpose à la fusion proprement dite.

V Structure du PCl^{B} liquide

Une réponse précise peut être donnée pour la structure du PCl^{B} liquide.¹³ Les règles de sélection donnent pour une bipyramide à base trigonale un spectre de six raies, dont deux polarisées, c'est-à-dire exactement le spectre du PCl^{B} liquide (nous avons vérifié que le spectre était complet et qu'une

¹⁰ H. Moureu, M. Magat et G. Wétroff, *C R*, 1936, 203, 257.

¹¹ W. Fischer et O. Juhemann, (*Z anorg allg Chem*, 1938, 235, 337) trouvent $100 \pm 1^\circ\text{C}$.

¹² voir un mémoire dans le Journal de Chimie Physique à paraître prochainement.

¹³ H. Moureu, M. Magat et G. Wétroff, *C R*, 1937, 203, 545.

prolongation de temps de pose par un facteur 4 n'augmentait pas le nombre de raies observées)

Les deux atomes de chlore des sommets ne sont donc pas entièrement équivalents aux trois chlores du plan de symétrie, qui contient aussi le phosphore. La dissociation en PCl^3 et Cl^3 , et la réaction avec les indones (à haute température), sont donc parfaitement compréhensibles (voir aussi Kapustinsky¹⁴)

Cette structure n'est pas en désaccord avec la structure électronique du phosphore. En effet, le phosphore possède comme électrons extérieurs deux électrons *s* et trois électrons *p*. Ces trois derniers sont responsables du phosphore trivalent. Pour que le phosphore devienne pentavalent, un des électrons *s* doit devenir électron *d* avec hybridisation, c'est-à-dire symétrisation des fonctions d'onde des électrons. La bipyramide à base trigonale présente les éléments de symétrie nécessaires.

Enfin, Monsieur Rouault¹⁵ a eu l'obligeance de nous communiquer les résultats de ses expériences inédites sur la diffraction des électrons par PCl^3 à l'état de vapeur. Il trouve lui aussi une structure symétrique en bipyramide. Rappelons, en outre, que Braun et Pinnow¹⁶ avaient conclu à cette même structure pour PF^3 gazeux.

VI La structure du PCl^3 solide¹⁸

Les conclusions sont beaucoup moins certaines en ce qui concerne le PCl^3 solide. En effet, comme la plupart des corps AX^3 que nous avons étudiés, PCl^3 absorbe la raie 4358 Å de Hg. on est alors obligé d'exciter le spectre Raman par la raie 5460 Å. Cette difficulté superposée à celle inhérente à tous les solides polycristallins ne nous permet d'affirmer, malgré l'accord avec Krishnamurti,⁹ que le spectre obtenu est bien le spectre complet. De même, les mesures de polarisation sont délicates et incertaines.

Nous n'avions d'autre ressource, pour étayer nos conclusions, que de comparer nos résultats à ceux que donne un composé ayant toutes chances de posséder la même structure que PCl^3 solide. Nous nous sommes adressé pour cela au SbCl^3 qui, à l'état liquide, présente effectivement un certain nombre de raies de fréquences très proches de celles observées sur PCl^3 solide (en particulier la fréquence 356 cm^{-1} , la plus intense, que l'on retrouve aussi pour NbCl_3 solide—Voir Tableau III)

¹⁴ Kapustinsky, *Z. Phys. Chem. B*, 1930, 8, 72.

¹⁵ Laboratoire de M. Jean Perrin.

¹⁶ *Z. Phys. Chem. B*, 1937, 33, 233.

Le SbCl^5 liquide a d'ailleurs été étudié par Redlich, Kurz et Rosenfeld¹⁷ qui ont observé quatre raies et attribuent à ce corps la structure d'une pyramide à base carrée. La théorie prévoit pourtant pour une molécule de cette symétrie neuf raies Raman, mais les auteurs précités ont admis que cinq d'entre elles étaient trop faibles pour apparaître sur leurs clichés.

En photographiant à notre tour le spectre de SbCl^5 liquide, et en sur-exposant dans l'espoir de faire apparaître les raies manquantes, nous n'avons observé qu'une raie supplémentaire, elle est intense mais très proche de la raie excitatrice et peut se confondre avec celle-ci sur des clichés à faible dispersion (Tableau III). D'autre part Mademoiselle Kurz¹⁸ a montré dans sa thèse qu'une des raies observées précédemment était double, et signale l'existence d'une raie 538 cm^{-1} . Ceci montre la complexité de la question et la nécessité de nouvelles expériences.

TABLEAU III

SbCl ⁵ liquide							PCl ⁵ solide		NbCl ⁵ solide Δν cm ⁻¹	TaCl ⁵ liquide Δν cm ⁻¹
Nouv			O Redlich		T Kurz		Δν cm ⁻¹	site		
Δν cm ⁻¹	Inten site	ρ	Δν cm ⁻¹	Inten site	Δν cm ⁻¹	Inten site				
72±4	10	6/7								115±5
177±3	7 (II)	6/7	178	2	{ 165±2 182±4	{ 2 3	244	4 (s)	170	175±5
309±2	5	?	304	2	305±2	4				.
356±2	10	P	355	2	356±1	7	356	10 (s)	356	
400±2	5	?	399	3	397±1	3	409	2 (s)	400	413±3
					538±1	1	450	8 (s)	427	(la plus intense)

Quoiqu'il en soit, la structure de SbCl^5 liquide et de PCl^5 solide proposée par Redlich et ses collaborateurs nous semble peu probable.

La structure qui nous paraît s'adapter le mieux aux faits est celle qui est en accord avec le schéma de Langmuir¹ un tétraédre PCl^4 , avec le cinquième atome de chlore en dehors du tétraédre, lié d'une façon semi-polaire, c'est-à-dire par une superposition de l'état ionique $\text{PCl}^{4+}\text{Cl}^-$ analogue

¹⁷ *Ibid.*, B, 1932, 19, 231.

¹⁸ T. Kurz, *Dissertation Vienne*, 1935, Communication privée.

à NH_4^+Cl^- et d'un état homéopolaire où l'un des cinq électrons jouerait un rôle différent des autres

Le tétraédre PCl_4 doit donner naissance, comme le prévoit la théorie, à quatre raies dont une polarisée ce sont ces quatre raies que l'on observe très aisément dans tous les clichés aussi bien de PCl_5 solide que de SbCl_5 liquide. Par contre la vibration $\text{PCl}_4 \leftrightarrow \text{Cl}$ doit se traduire par une raie de fréquence faible en raison de la grande masse du tétraédre PCl_4 , et peu intense à cause de la liaison ionique. Mais la superposition à la liaison ionique d'une liaison homéopolaire doit provoquer une augmentation de l'intensité de cette vibration ainsi que la destruction de certaines dégénérescences par passage de la symétrie T_d à la symétrie C_{3v} . Les deux effets, non décelables sur le PCl_5 solide semblent se manifester sur le SbCl_5 liquide on observe en dehors des quatre raies correspondant au tétraédre une raie de faible fréquence (72 cm^{-1}), la raie 177 cm^{-1} est dédoublée, et il semble apparaître une nouvelle raie à 538 cm^{-1} .

La structure que nous proposons pour PCl_5 solide (et pour SbCl_5 liquide) est compatible avec la structure quadratique du réseau cristallin. La différence de types de liaison entre le solide et le liquide permet en outre d'expliquer le fait remarquable pour un conducteur non métallique que la conductibilité du $\text{PCl}_5^{(4)}$ soit plus grande à l'état solide qu'à l'état liquide.

VII Moment électrique

Il subsiste une difficulté en ce qui concerne le moment électrique en effet le PCl_5 liquide doit, en raison de sa structure symétrique, posséder un moment électrique nul, tandis que le PCl_5 solide devrait avoir un moment électrique important à cause de la forte contribution de la liaison ionique. Or les mesures de Trunel (5) donnent un moment de 0,87 D en utilisant des solutions de PCl_5 dans CCl_4 à température ordinaire, pour lesquelles l'effet Raman ne laisse apparaître que les raies correspondant à la structure du PCl_5 liquide. On calcule le même moment à partir de l'indice de réfraction et de la constante diélectrique du PCl_5 liquide et un moment légèrement supérieur à partir de ces mêmes données pour le solide, en supposant que toutes les molécules de solide puissent s'orienter librement dans le champ électrique. Comme cette hypothèse est sûrement erronée dans le cas du solide avec des molécules à fort moment électrique, le calcul sur le solide ne peut donner qu'un moment électrique apparent, le moment réel devant être sensiblement plus élevé.

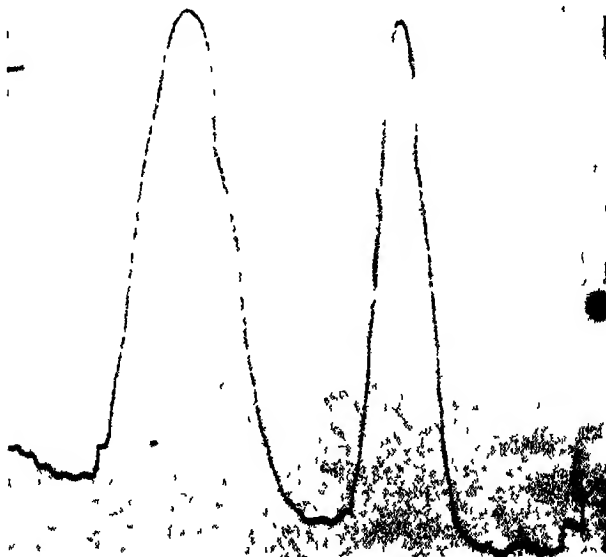
Pour expliquer ces anomalies on est conduit à admettre qu'en phase homogène, c'est-à-dire à l'état liquide ou en solution, il existe un état d'équilibre entre les deux formes correspondant aux structures "solide" et

"liquide" du PCl^5 , équilibre qui doit être fortement déplacé en faveur de la forme liquide. Le moment électrique mesuré serait donc le moment "apparent" du mélange. Le calcul montre alors qu'il suffit de la présence de 3% de molécules possédant un moment de l'ordre de 6 D, dans un milieu à moment électrique nul, pour que le moment apparent du mélange soit de l'ordre de 1 D.

Cette hypothèse d'un état d'équilibre, que nous nous proposons d'ailleurs de vérifier dans de nouvelles expériences, apparaît toute naturelle puisqu'il ressort implicitement de nos travaux qu'il doit exister à 160° un point de transformation pour le PCl^5 .

VIII La rotation libre

Nous avons microphotométrié les raies 271 et 392 cm^{-1} du PCl^5 liquide avec différentes démultiplications du microphotomètre. Tandis qu'à faible démultiplication les raies ont l'aspect de courbes de Gauss, à grande démultiplication on voit apparaître des maxima secondaires, correspondant aux branches de rotation (voir cliché 1). Ces maxima sont deux fois plus écartés



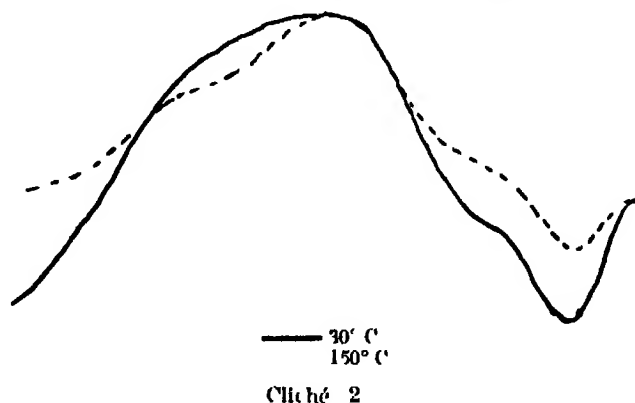
Cliché 1.

de la branche Q pour la vibration dépolarisée que pour la vibration polarisée, comme le prévoit la théorie de Teller et Tisza¹⁰. L'écartement est d'autre part trop grand pour pouvoir s'expliquer par l'effet des isotoopes de chlore

¹⁰ Z f Physik, 1932, 73, 791.

En comparant ces ailes de rotation avec les courbes théoriques établies pour les molécules polyatomiques à l'état gazeux par Plazcek et Teller,²⁰ on constate que la position des maxima est bien compatible avec l'ordre de grandeur du moment d'inertie calculable à partir de notre modèle. Par contre, il ne nous a pas été possible d'ajuster la forme des courbes théoriques de manière à déterminer le rapport des moments d'inertie. En particulier l'intensité des branches antistokes paraît être plus faible que celle prévue par la théorie qui n'est d'ailleurs valable que pour les gaz.

Dans le spectre du solide les bandes Raman sont trop faibles pour que l'on puisse analyser leurs structures, on a donc étudié le voisinage de la raie excitatrice. Le cliché 2 montre nos résultats pour deux températures différentes, 30 et 150°. Il semble bien qu'une rotation apparaisse entre ces deux



températures, la bande antistokes ne se manifestant qu'à la température supérieure. L'analyse thermique a d'ailleurs fait ressortir la présence dans le PCl_5 solide, vers 115°, d'un point de transformation de deuxième ordre, qui correspond probablement à l'apparition de cette rotation.²¹

IX Spectre Raman de NbCl_5 et de TaCl_5 ⁽²¹⁾

Nos recherches ont été étendues à d'autres chlorures de la même série. De ces expériences qui ne sont pas encore terminées, nous détachons simplement les premiers résultats relatifs aux spectres de NbCl_5 solide (le liquide fortement coloré en rouge marron n'a pas pu être étudié) et de TaCl_5 liquide. Le spectre de NbCl_5 solide est très voisin de celui de PCl_5 solide, sa structure devrait donc être analogue, ce qui n'a rien d'étonnant étant donnée sa configuration électronique (électrons extérieurs $4p^4, 5s^1$).

²⁰ *Ibid.*, 1933, 81, 209

²¹ avec M. Pierre Süe

DURCHRECHNUNG EINIGER AUSGEWÄHLTER MOLEKÜL-MODELLE.

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(Mit 9 Text-Figuren)

Es werden Frequenz, Schwingungs-Form und Energie-Verteilung für die ebenen Schwingungen einiger Valenzkraft-Systeme in Abhängigkeit von den Modell-Konstanten (Massen, Winkel, Federkräfte) berechnet. In Tabellen und Figuren werden die Ergebnisse für die folgenden Modelle mitgeteilt: 1, 3, 5-substituiertes Benzol C_6X_3 , tetra-substituiertes Äthylen $X_2C=CX_2$, *cis*- und *trans*-substituiertes Äthylen $X-C=C-X$, Phosgen-Typus $X \cdot CO \cdot X$.

I DER Molekül-spektroskopiker wird bei der vergleichenden Betrachtung der Schwingungs-spektren von räumlich gleichartig gebauten Molekülen (Beispiel $H_3C \cdot H_2C \cdot X$ mit $X = Cl, Br, J$) immer wieder vor die Notwendigkeit gestellt, sich einen Ueberblick darüber zu verschaffen, wie sich beim zugehörigen Modell die Frequenzen bei Variation irgend eines der Modell-Parameter ändern. Dabei sind die Frequenz-Quadrate als Wurzeln von Gleichungen meist höheren Grades (je nach der Zahl der Schwingungsformen, die zum gleichen Symmetrie-Typus gehören) zu bestimmen, deren Koeffizienten häufig unübersichtliche Funktionen der Modell-Konstanten (Massen, deren räumliche Verteilung und die sie zusammenhaltenden Federkräfte) sind. Daher stösst schon bei einer Frequenz-Gleichung von nur zweitem Grad die allgemeine diesbezügliche Diskussion auf Schwierigkeiten, bei Gleichungen von höherem als zweiten Grad dürfte die direkte numerische Auswertung, so lastig und zeitraubend sie auch sein mag, immer noch schneller zum Ziele führen, als die allgemeine Behandlung, sofern letztere überhaupt durchführbar ist.

Dies war der Grund dafür, daß im hiesigen Institut die systematische Durchrechnung einfacher Modelle durchgeführt wurde, wobei Frequenzhöhe, Schwingungs-Form und Verteilung der potentiellen Energie auf die einzelnen Bindungen zu bestimmen waren, alles als Funktion passend gewählter, varrierender Modell-Parameter (meist der Substituenten-Masse). Dabei wurden so eigenartige und oft ganz unerwartete Ergebnisse erhalten, daß ihre Veröffentlichung gerechtfertigt sein dürfte. Ein Teil der Resultate wurde schon in früheren Publikationen gelegentlich verwertet; über die der Zeit nach ersten Rechnungen wird im Folgenden berichtet. In allen Fällen

handelt es sich dabei um "Valenzkraft-Systeme" und um die in der Modell-Ebene ausgeführten sog. "ebenen" Schwingungen

II Die totalsymmetrischen Schwingungen des Modelles von 1, 3, 5-substituierten Benzol C_6X_3 (ohne H-Atome in Stellung 2, 4, 6) Die bekannte Tatsache, daß die Schwingungs-Spektren von symm $C_6H_3X_3$ eine ganz überraschend lagenkonstante starke Linie um 1000 cm^{-1} aufweisen, wurde von K W F Kohlrausch¹ in ganz allgemeiner Weise erklärt und letztlich und schließlich darauf zurückgeführt, daß schon im nicht substituierten Benzol C_6H_6 zwei trigonal symmetrische Schwingungen infolge der speziellen dynamischen Verhältnisse die nahezu gleichen Frequenzen 992 und 1008 aufweisen. Es war nun von Interesse nachzusehen, einerseits inwieweit die modellmäßige Beschreibung diesen Verhältnissen quantitativ Rechnung tragen kann, andererseits, wie die Schwingungsform beschaffen ist, die trotz zweifellos eintretender Veränderungen doch stets zur selben Frequenz führt.

Die von Trenkler² abgeleiteten Frequenzformeln für die drei trigonal symmetrischen Schwingungen des Modelles C_6X_3 lauten ($n_i^2 = 5,86 \cdot 10^{-2} \omega_i^2$)

$$n_1^2 + n_2^2 + n_3^2 = f \frac{m + M'}{mM'} + (F + 12D) \frac{M + M'}{2MM'}$$

$$n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2 = \frac{1}{2} f (F + 12D) \left(\frac{1}{mM'} + \frac{1}{m\bar{M}} + \frac{1}{MM'} \right) + 12DF \frac{1}{MM'}$$

$$n_1^2 n_2^2 n_3^2 = 12FfD \frac{1}{m\bar{M}M'}$$

Ueber die Zuordnung der Zeichen F , f , D zu den Federkräften, M , M' , m zu den Massen des Modelles vergleiche Figur 3. Zur Auswertung obiger Formeln wurden die folgenden, den Verhältnissen im Molekül angepassten³ Zahlenwerte verwendet: $F = 7,65$, $f = 4,45$, $D = 0,65 \cdot 10^6 \text{ Dyn/cm}$, $M = 13$ (entsprechend C + H), $M' = 12$, $m = \text{variabel}$. Die Besonderheit der hier obwaltenden Verhältnisse erhält z. B. daraus, daß sich das Rechnen mit funfstelligen Logarithmen als unzulänglich erwies und daß selbst die Genauigkeit von siebenstelligen Logarithmen in den besonders empfindlichen Fällen mit $m < 1$ nicht hinreichte (Der zur Auflösung der kubischen Gleichung einzuführende Winkel-cosinus wird grösser als Eins). Die Ergebnisse der Rechnung sind zahlenmassig in Tab. 1 und zeichnerisch in den Figuren 1, 2, 3 zusammengestellt.

¹ K W F Kohlrausch, *Naturwiss.*, 1937, **25**, 635.

² F Trenkler *Physikal. Ztschr.* 1936, **37**, 838.

³ K W F Kohlrausch, "Bericht über die Spektren der Benzol-Derivate," *Physikal. Ztschr.*, 1936, **37**, 58.

TABELLE I

Frequenz-Werte sowie Potential-Anteile der Federkräfte F , f , D für die total-symmetrischen Schwingungen des Modelles C_6X_2

		$m = 1$	$m = 2$	$m = 4$	$m = 8$	$m = 15$	$m = 30$	$m = \infty$
ω_1	$\omega =$	2884	2151	1707	1486	1397	1347	1316
	$\tau (F)$	0.67	2.68	8.82	18.15	24.4	28.6	31.3
	$\tau (f)$	98.8	94.6	82.55	63.5	50.8	41.9	36.2
	$\tau (D)$	0.67	2.68	8.87	18.5	24.9	29.6	32.5
ω_2	$\omega =$	1009.4	1007.1	1006.8	1006.7	1006.7	1006.7	1006.7
	$\tau (F)$	7.56	42.5	48.0	49.6	50.3	50.7	51.0
	$\tau (f)$	0.32	0.04	0.02	0.03			
	$\tau (D)$	92.2	57.5	52.0	50.4	49.5	49.4	49.0
ω_3	$\omega =$	1000	949	846	687	531	357	
	$\tau (F)$	92.3	53.1	43.7	32.8	26.0	21.6	18.3
	$\tau (f)$	0.99	5.25	17.3	36.1	48.9	57.5	63.6
	$\tau (D)$	6.84	39.75	39.0	31.2	25.2	21.0	17.9

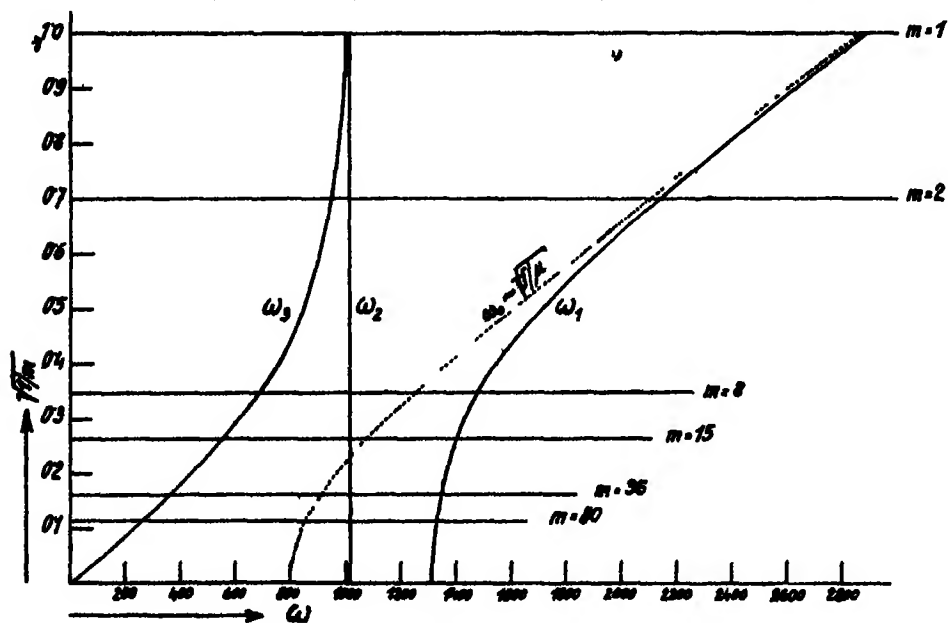


FIG 1

Die Frequenzen ω_1 , ω_2 , ω_3 , der trigonal symmetrischen Schwingungsformen von 1, 3, 5- C_6X_2 in Abhängigkeit von der Masse m des Substituenten X (voll ausgezogene Kurven). Die Eigenfrequenz $\omega_0 \sim \sqrt{1/\mu}$ der Substituentenbindung liegt auf der punktierten Kurve.

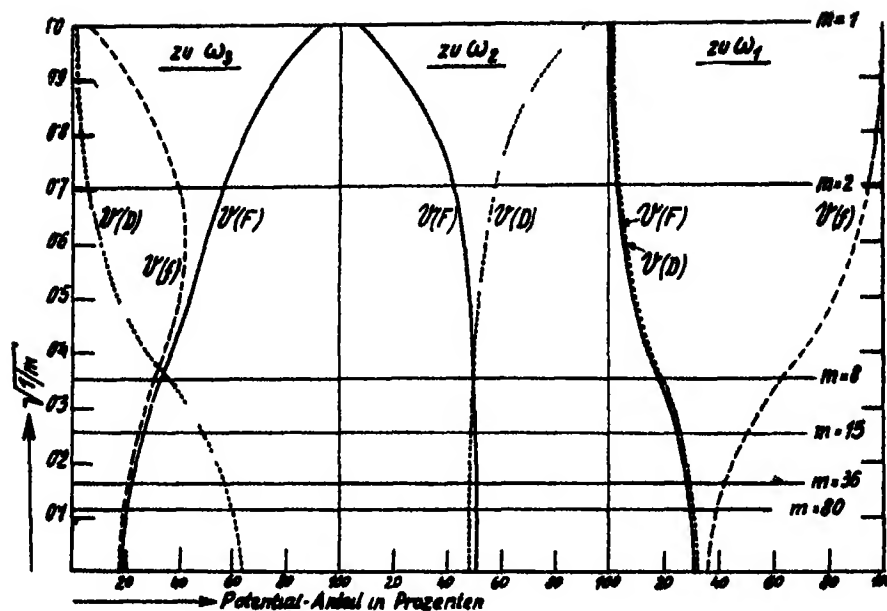


FIG 2

Die prozentuellen Anteile $v(F)$ [voll ausgezogen], $v(f)$ [gestrichelt], $v(D)$ [punktuiert] der Gesamt-Energie, die auf die Beanspruchung der Federkräfte F, f, D jeweils verwendet werden

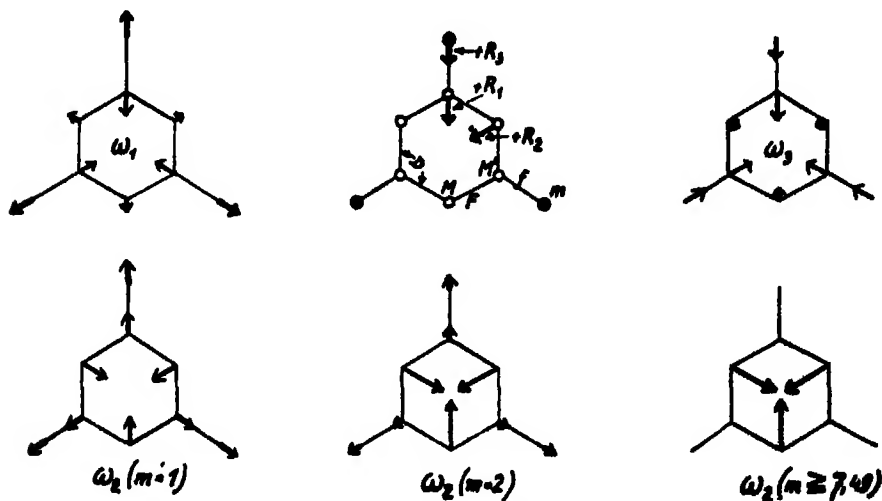


FIG 3

Die zu $\omega_1, \omega_2, \omega_3$ gehörigen Schwingungsformen (schematisiert, da sich die wahren Größenverhältnisse der Amplituden mit zeichnerischen Mitteln kaum darstellen lassen).

Aus Tab 1 und den Figuren 1, 2, 3 hest man ab

ω_1 variiert für $m = 0$, bzw $m = 1$, bzw $m = \infty$ von $\omega = \infty$ über $\omega = 2884$ bis $\omega = 1316$, für kleine Massen m ($m < 3$) steckt (vergl Fig 2) nahezu die ganze Energie der Schwingungs-Bewegung in der Feder f , so daß hier ω_1 für die Substituenten-bindung "charakteristisch" ist, dementsprechend verläuft hier die Kurve für ω_1 (vergl Figur 1) parallel mit der die Eigenfrequenz ω_0 der CX-Bindung beschreibenden punktierten Kurve. Die Schwingungsform bleibt für alle m im wesentlichen die gleiche R_1 ist (vergl Fig 3) stets in Gegenphase mit R_2 und R_3 , deren Elongationen mit zunehmender Masse m abnehmen.

ω_2 variiert für $m = 0$, bzw $m = 1$, bzw $m = \infty$ von $\omega = 1006$ über $\omega = 1000$ bis $\omega = 0$. Für kleine Werte von m handelt es sich im wesentlichen um eine Valenzschwingung des Ringes C_6 , da nach Fig 2 der Haupt-Teil der Energie für die Beanspruchung der Feder F verbraucht wird, für $m = 1$ wird daher fast nichts an den Winkeln geändert, das heisst, es handelt sich um eine fast (für $m = 0$ um eine vollkommen) reine Pulsationsbewegung des C_6 -Ringes. Auch bei ω_2 ändern sich mit zunehmendem m nur die Amplituden-, nicht die Phasen-Verhältnisse, erstere allerdings derart, daß (vergl Fig 2) für große m mehr Energie auf Winkel-als auf Längen-Änderungen aufgewendet und dadurch allmählich der Charakter einer Deformations-Schwingung erreicht wird.

ω_3 variiert erstaunlich wenig und bleibt für $m > 8$ überhaupt konstant. Für kleine Massen m handelt es sich nach Fig 2 um eine fast (für $m = 0$ um eine vollkommen) reine Deformationsschwingung, da $\nu(D)$ den Hauptanteil der Energie darstellt. Für $m = \infty$ wird etwa gleichviel Energie in $\nu(F)$ und $\nu(D)$ vorgefunden, während $\nu(f)$ verschwindend klein ist. Die Variation des Substituenten bewirkt eine Veränderung der Schwingungsform (Fig 3) und damit eine verschiedene (beinahe "komplementäre") Beanspruchung (Fig 2) der den Ring charakterisierenden Federkräfte F und D . Die Elongationen R_1 und R_2 sind zunächst gegenphasig, für $m = 7,49$ wird $R_1 = 0$, für $m > 7,49$ wird R_1 mit R_2 gleichphasig, aber vernachlässigenswert klein, so daß f unbeanspruch bleibt.

Man wird zugeben müssen, daß es sich hier um ein interessantes und lehrreiches Schwingungs-Beispiel handelt.

III Die Raman-aktiven ebenen Schwingungen (Sym Typ A_{1g} , B_{1g}) des Modells für vierfach substituiertes Äthylen $X_2C CX_2$. Die für ein Valenzkraftsystem vom Äthylen-Typus gültigen Formeln sind im Ergänzungsband des SRE p 73 angegeben. Es wurden die Frequenzen, die relativen Amplituden und mit Hilfe der letzteren die prozentuelle Aufteilung der potentiellen Energie berechnet, die auf die Distanz-erhaltenden Kräfte

F und f bzw winkelerhaltenden Krafte $D = 2 d_2 + \frac{s_2}{s_1} d_1$ und d_1 entfallen (Bezüglich der Zuordnung der Symbole $F, f, d_1, s_1, s_2, M, m$, vergleiche man Figur 5) Es wurden die folgenden, dem Spektrum des Aethylens selbst möglichst eine vollkommene Anpassung ist mit vernünftigen Winkel-Werten nicht möglich- angepassten Zahlenwerten gerechnet, $F = 8,94$, $f = 4,85$, $D = 1,20 \cdot 10^8 \text{ Dyn/cm}$, $d_1 = d_2$, $s_1 = 1,1$, $s_2 = 1,34 \cdot 10^{-8} \text{ cm}$, $2 \beta = 110^\circ$, $M = 12$, $m = \text{variabel}$ Die Ergebnisse sind zahlenmassig in Tabelle 2 und zeichnerisch in Figur 4 and 5 zusammengestellt

TABELLE II

Frequenz-Werte sowie Potential-Anteile der Federkraft, F, f, D der ebenen, Raman-aktiven Schwingungen des Modelles $X_2C \cdot CX_2$

		$m = 1$	$m = 2$	$m = 8$	$m = 15$	$m = 36$	$m = 80$	$m = \infty$
ω_1	$\omega =$	2980	2208	1854	1823	1806	1800	1796
	$v(F)$	2 08	17 30	08 04	74 00	77 05	78 30	78 95
	$v(f)$	97 00	80 45	24 85	18 86	15 86	14 80	14 02
	$v(D)$	0 45	2 42	7 12	7 24	7 18	7 14	7 09
ω_2	$\omega =$	1733	1533	919	681	443	298	
	$v(F)$	51 45	62 05	21 20	16 17	13 72	13 39	
	$v(f)$	2 08	10 40	74 95	80 95	83 65	82 18	
	$v(D)$	45 55	17 70	3 93	2 92	2 45	2 38	
ω_3	$\omega =$	1266	943	481	352	228	154	
	$v(F)$	45 75	19 80	10 87	9 98	8 99	7 40	
	$v(f)$	0 48	0 27	0 10	0 15	0 14	0 12	
	$v(D)$	53 95	79 75	89 00	90 00	90 98	92 55	
ω_4	$\omega =$	3045	2281	1526	1394	1308	1275	1249
	$v(F)$							
	$v(f)$	99 05	96 65	81 20	72 85	65 40	62 55	61 0
	$v(D)$	0 95	3 25	18 80	27 15	34 60	37 45	39 0
ω_7	$\omega =$	1155	939	603	468	316	215	
	$v(F)$							
	$v(f)$	1 00	3 05	18 55	27 00	34 8	37 45	
	$v(d)$	99 00	96 95	81 45	73 00	65 2	62 55	

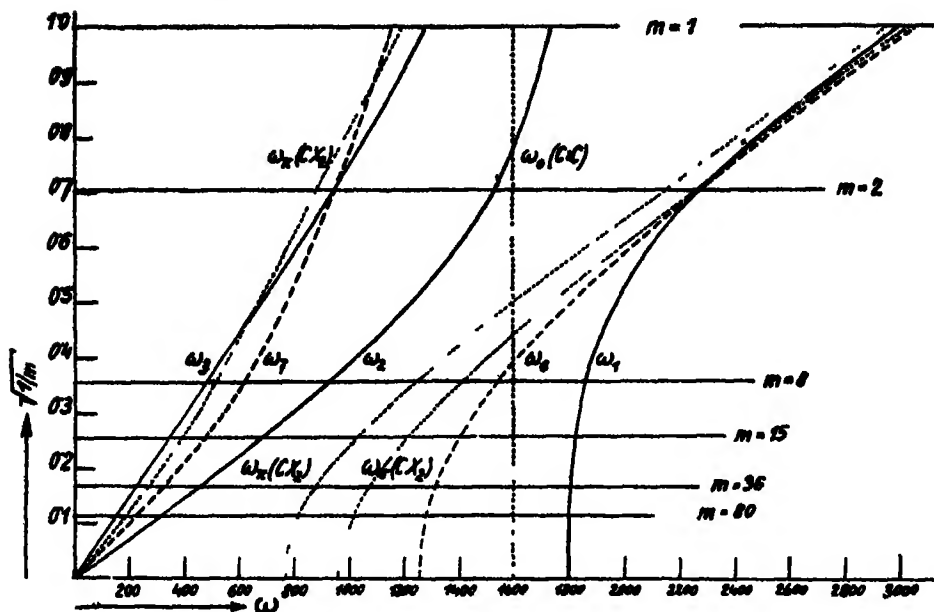


FIG 4

Die Frequenzen ω_1 , ω_2 , ω_3 der totalsymmetrischen (Typus A_{1g} , voll ausgezogene Kurven) und ω_4 , ω_5 , ω_6 , ω_7 der ebenen, aber sonst antisymmetrischen (Typus B_{1g} , gestrichelte Kurven) Schwingungen von $X_2C \cdot CX_2$ in Abhängigkeit von der Masse m des Substituenten X . Auf den punktierten Kurven liegen die Eigenfrequenzen ω_0 ($C=C$) der Doppelbindung bzw. die drei Eigenfrequenzen ω_n , ω_n , ω_σ der CX_2 -Gruppe.

Aus den Figuren 4, 5 und aus Tabelle 2 folgt

ω_1 Für kleine m ist ω_1 charakteristisch für die symmetrische Valenzfrequenz der CX_2 -Gruppe ($\nu(f) \sim 90\%$), für größere m steckt der Hauptanteil der Energie in der Doppel-Bindung, d. h. ω_1 wird charakteristisch für die $C:C$ -Bindung.

ω_2 Für kleine m ist ω_2 zu gleichen Teilen $C-C$ - und Deformations-Schwingung, für mittlere m verläuft die ω_2 -Kurve ungefähr parallel mit der punktierten Kurve für die Valenzschwingung ω_σ (CX_2).

Dem Gange von ω_1 und ω_2 entspricht es, wenn als sogenannte " $C-C$ Frequenz" beobachtet wird. Für $H_2C \cdot CH_3$, $\omega = 1623$, für $D_2C \cdot CD_3$, $\omega = 1515$, diese beiden Werte gehören zur ω_2 -Schwingung. Für $(H_2C)_2$, $C:C$ (CH_3) $_2$, $\omega = 1676$, für $Cl_2C \cdot CCl_2$, $\omega = 1589$, die beiden letzten Werte gehören zur ω_1 -Schwingung. Zwischen $D_2C \cdot CD_3$ und $(H_2C)_2$, $C:C$ (CH_3) $_2$ findet daher scheinbar ein Sprung der $C-C$ -Frequenz zu höheren Werten statt.

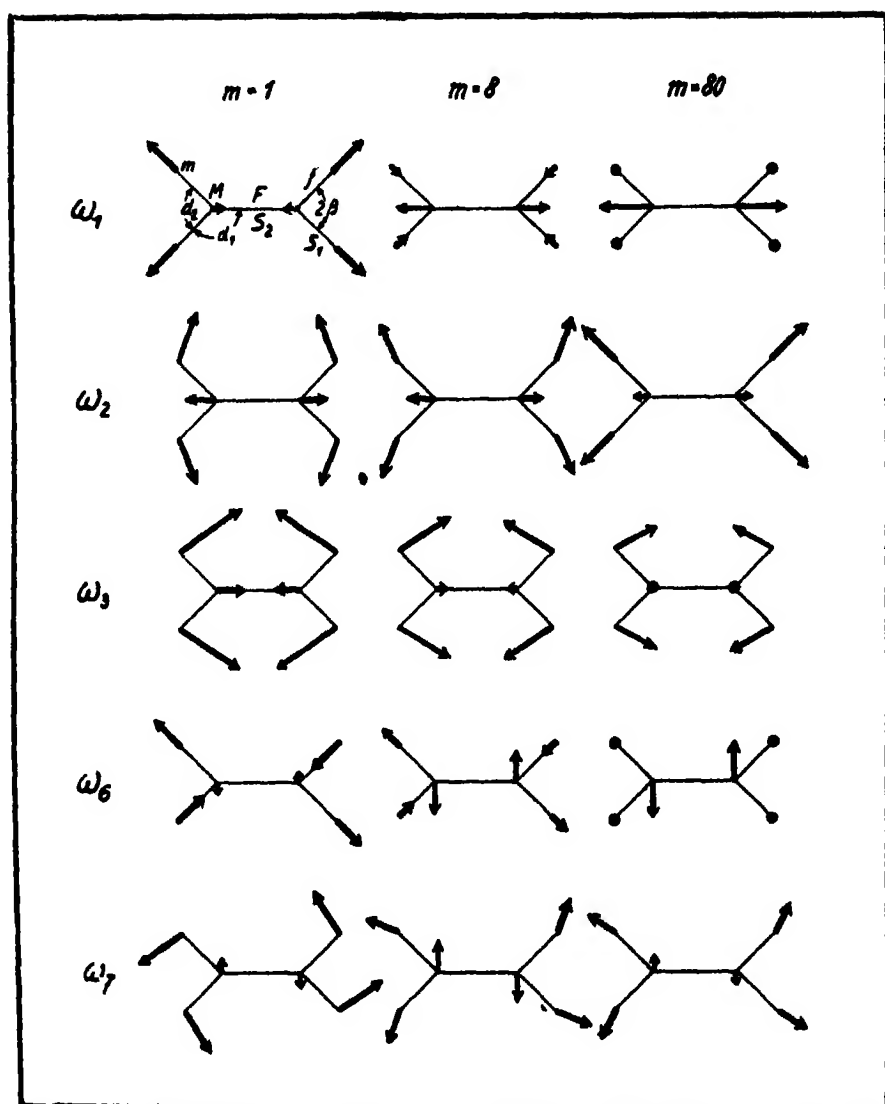


FIG. 5

Die zu den Frequenzen $\omega_1, \omega_2, \omega_3, \omega_6, \omega_7$ der Fig. 4 gehörigen Schwingungsformen (schematisiert) für die Fälle $m = 1, m = 8, m = 80$

ω_3 Für kleine Werte von m handelt es sich um eine "gemischte" für große m um eine reine Deformations-Schwingung, die nach ihrem Frequenzgang als charakteristisch für die symmetrische Deformations-Schwingung ω_π (CX₂) der CX₂-Gruppe angesehen werden kann

ω_6 Für kleine m eine reine Valenzschwingung der CX_2 -Gruppe [$\nu(f) > 80\%$] und infolge ihres mit $\omega\sigma(CX_2)$ parallelen Verlaufes für die CX_2 -Gruppe charakteristisch Für große m ist dies nur mehr in grober Näherung der Fall

ω_7 Für kleine m eine reine Deformations-Schwingung [$\nu(d) > 80\%$], später eine gemischte Schwingung Aus Symmetrie-Gründen darf bei ω_6 und ω_7 die Feder F nicht auf Dehnung beansprucht werden, daher ist in beiden Fällen für alle m -Werte $\nu(F) = 0$

IV Die ebenen Ketten-Schwingungen von *cis*- und *trans*-substituiertem Äthylen $X-C-C-X$ Die Frequenzgleichungen für diese beiden Fälle wurden zuerst von Lechner abgeleitet, man findet sie zum Beispiel in S R E Erg Bd p 67/68 Sie wurden ausgewertet für $F = 9,36 \cdot 10^5$, $f = 4,68 \cdot 10^5$, $d = 0,4 \cdot 10^5$ Dyn/cm, $\beta = 180^\circ$, $\alpha = 55^\circ$, $M = 13$ (entsprechend C-H), m variabel Ueber die Ergebnisse vergleiche Tabelle 3 und Figur 6, Schwingungsformen z B in Figur 8

TABELLE III.

Die Frequenzen der ebenen Ketten-Schwingungen des Modells von *cis*- und *trans*-substituiertem Äthylen $XC-CX$

		$m = 1$	$m = 2$	$m = 8$	$m = 15$	$m = 36$	$m = 80$	$m = \infty$
<i>cis</i>	ω_1	2946	2195	1697	1671	1658	1654	1650
	ω_2	1558	1512	1110	925	769	693	632
	ω_3	827	592	308	233	155	124	
	ω_4	2934	2151	1287	1119	992	942	903
	ω_5	1027	838	635	569	503	466	427
<i>Trans</i>	ω'_1	2947	2197	1679	1665	1653	1649	1646
	ω'_2	1566	1526	1187	1034	932	893	862
	ω'_3	990	795	537	435	304	210	
	ω'_4	2932	2146	1270	1071	914	845	784
	ω'_5	857	627	371	313	267	247	229

In Bezug auf ω_1 sind *cis* und *trans* praktisch ununterscheidbar, für kleine m ist ω_1 bzw. ω'_1 charakteristisch für die Bindung CX , für große m charakteristisch für die $C-C$ -Bindung, deren Eigenfrequenz ω_6 auf der punktierten vertikalen Geraden liegt Ebenso ist in Bezug auf ω_4 bzw. ω'_4 der Unterschied zwischen *cis* und *trans* nur gering, da $\omega'_4 \sim \sqrt{f/\mu}$ ist, ist diese

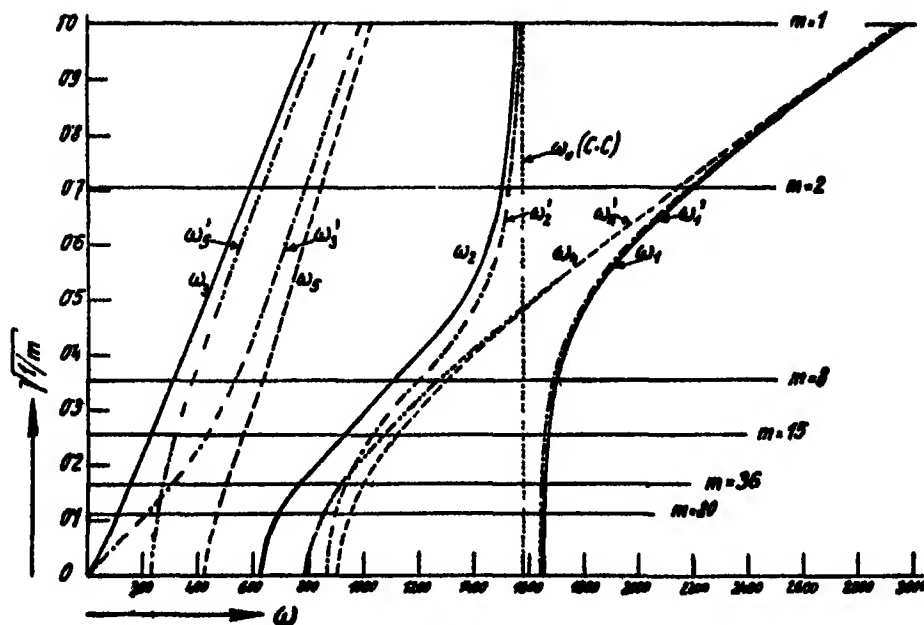


FIG. 6.

Die Frequenzen der ebenen Ketten-Schwingungen von $\text{X}-\text{C}-\text{C}-\text{X}$ bei variabler Masse m des Substituenten X .

cis-Form: symm. $\omega_1, \omega_2, \omega_3$ —————, antisymm ω_1, ω_3 - - - - -
trans-Form: symm. $\omega_1', \omega_2', \omega_3'$ - · - · - ·; antisymm ω_1', ω_3' - · - · - ·

Frequenz identisch mit der Eigenfrequenz der $\text{C}-\text{X}$ -Bindung. Bei ω_2 bzw. ω_3' ist der Unterschied zwischen beiden Formen schon merklich, für kleine m sind diese Frequenzen für die $\text{C}-\text{C}$ -Bindung charakteristisch. Dem Frequenzgang von ω_2 (ω_3') und ω_1 (ω_1') entspricht es, wenn im Molekülspektrum von $\text{DHC}-\text{CHD}$ für *cis* und *trans* $\omega' = \omega = 1567$, dagegen in $\text{H}_3\text{C}-\text{HC}-\text{CH}-\text{CH}_3$ trotz schwererem Substituenten höhere Werte gefunden werden. Der Modell-Rechnung entspricht es jedoch nicht, daß in Dimethyläthylen die *cis* Form mit $\omega = 1658$ eine merklich niedrigere $\text{C}-\text{C}$ -Frequenz aufweist als die *trans*-Form mit $\omega' = 1674$, auch die starke Erniedrigung auf $\omega_1 = 1586$ bzw. $\omega_1' \times 1576$ in Dichlor- und $\omega_1 = 1584$ bzw. $\omega_1' = 1578$ in Dibrom-äthylen entspricht nicht der Modellrechnung. Hier dürfte eine Änderung in der Konstitution der $\text{C}-\text{C}$ -Bindung eingetreten sein.

Der stärkste Unterschied zwischen *cis* und *trans* stellt sich bei den tiefen Deformations-Frequenzen ω_3 und ω_3' ein: für *cis* ist $\omega_3 > \omega_3'$, für *trans* (wenn man von den Substituenten mit großem m absieht) umgekehrt $\omega_3' < \omega_3$.

V Die ebenen Schwingungen verschieden gewinkelter Vierer-Ketten mit konjugierter Doppelbindung $O\ HC\ CH\ O$ Mit den gleichen Frequenz-Formeln wie im vorhergehenden Fall (S R E Erg Bd p 67/68) wurde folgendes Beispiel gerechnet $F = 4,45$, $f = 10,0$, $d = 0,4 \cdot 10^8$ Dyn/cm, $M = 13$ entsprechend $C + H$, $m = 16$ entsprechend O , $\beta = 180 - \alpha$ variabel zwischen 0° (lineares System) und 90° Ergebnisse in Tabelle 4 und Figur 7 und 8

TABELLE IV

Frequenz-Werte und Potential-Anteile der Federn für die ebenen Schwingungen verschieden gewinkelter vierer-Ketten mit konjugierter Doppelbindung

cw form				linear		trans form		
$\beta = 90^\circ$	$\beta = 60^\circ$	$\beta = 30^\circ$		$\beta = 0$		$\beta = 30^\circ$	$\beta = 60^\circ$	$\beta = 90^\circ$
1542	1625	1734	ω_1	1775	ω_1'	1736	1640	1583
100	84.6	74.6	ϵ (f)	72.0	ν (f)	74.8	85.0	91.7
	15.3	25.4	ν (F)	28.0	ν (F)	24.8	12.5	0.2
	0.1		ν (d)		ν (d)	0.4	2.5	6.1
1106	970	752	ω_2	629	ω_2'	518	417	352
	15.1	24.7	ν (f)	28.0	ν (f)	13.6	8.4	4.9
95.5	80.1	70.5	ϵ (F)	72.0	ν (F)	29.0	13.6	4.9
4.5	4.8	4.8	ϵ (d)		ν (d)	57.4	78.0	90.2
202	217	264	ω_3	308	ω_3'	308	308	308
	0.4	0.9	ν (f)		ν (f)			
5.0	4.6	3.8	ν (F)		ϵ (F)			
95.0	95.0	95.3	ν (d)	100	ν (d)	100	100	100
1582	1574	1554	ω_4	1542	ω_4'	1542	1512	1542
94.6	95.3	98.2	ν (f)	100	ν (f)	100	100	100
			ν (F)		ν (F)			
5.4	4.7	1.8	ν (d)		ν (d)			
424	557	672	ω_5	717	ω_5'	866	1045	1105
5.5	4.8	1.9	ν (f)		ν (f)	11.5	6.6	0.9
			ν (F)		ν (F)	45.4	74.0	94.8
94.5	95.2	98.1	ν (d)	100	ν (d)	43.1	19.4	4.3

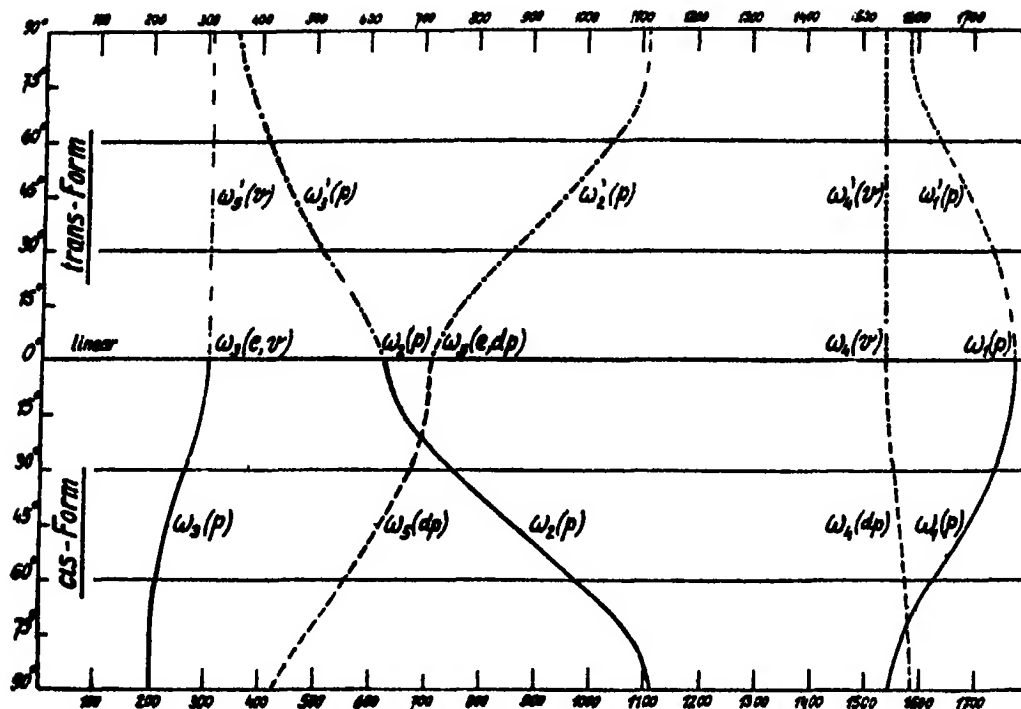
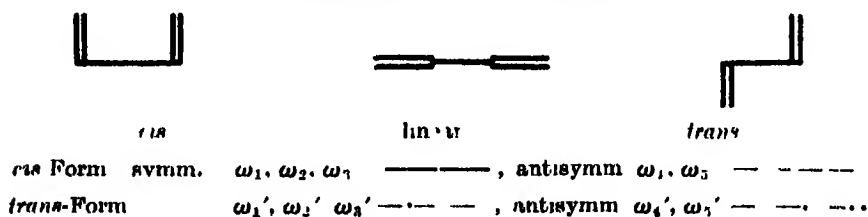


FIG. 7

Die Frequenzen der oberen Vierer-Kette $O-H-C-Cl-O$
beim Uebergang zwischen den Formen



Im Allgemeinen ist zu diesem Modell und zu der Auswirkung seiner Veränderung auf das Schwingungs-Spektrum zu bemerken. Die spektrale Verschiedenheit der *cis*- und *trans*-Form äußert sich in Figur 7 darin, daß deren untere und obere Hälfte nicht symmetrisch bezüglich der Achse $\beta = 0$ sind, am geringsten ist der Unterschied wieder zwischen ω_1 und ω_1' bzw. zwischen ω_4 und ω_4' . Beim Durchgang durch $\beta = 0$ tritt, abgesehen von ω_1 und ω_8 , eine sprunghafte Änderung in den Auswahl Regeln ein, diese sind in Fig. 7 und 8 durch die in Klammern beige-setzten Zeichen *p* (polarisiert), *dp* (depolarisiert), *v* (verboten) angedeutet.

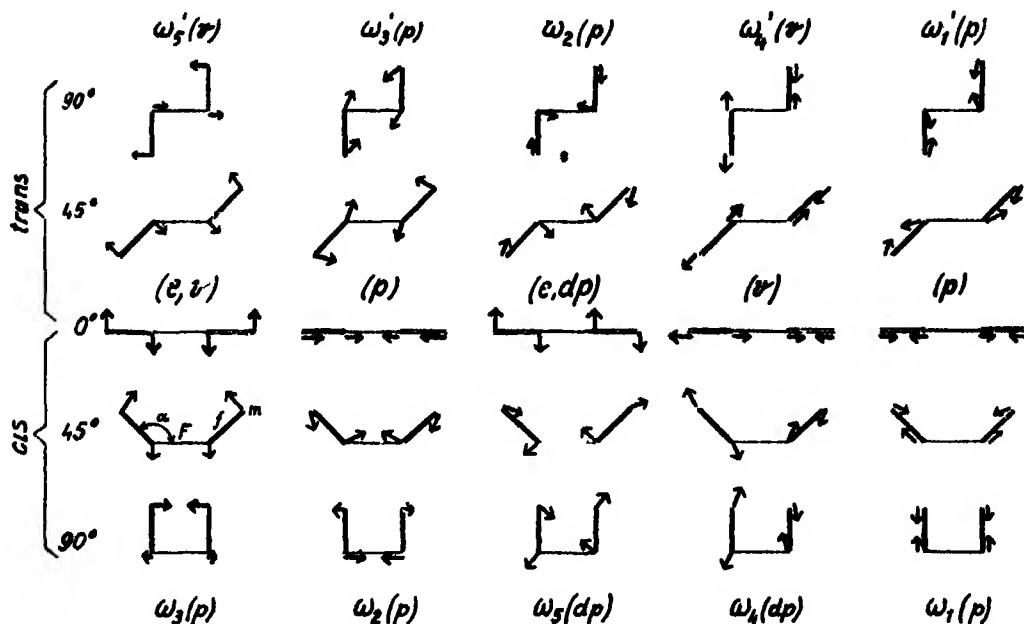


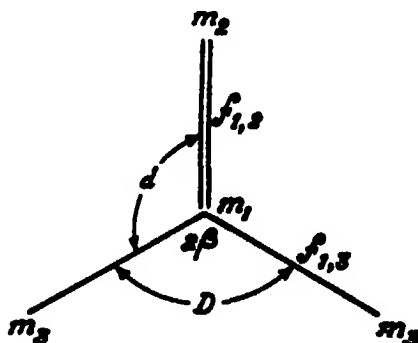
Fig 8

Schematisierte Schwingungs-Formen zu den Frequenzen der Fig 7

Im Einzelnen sei auf Folgendes verwiesen. Bei ω_1 , ω_4 , ω_5 wird der Charakter als Valenz bzw. Deformations-Schwingung unabhängig von β beibehalten, ω_3 dagegen gehört in der *cis* und linearen Form zu einer vorwiegend die Bindung C-C beanspruchenden Valenz-Schwingung und wird in der *trans*-Form zur Deformations-Schwingung ω'_3 . Umgekehrt gehört ω_5 in der *cis*- und linearen Form zu einer Deformations-Schwingung und geht in der *trans*-Form bei grösserem β über zu der die Feder F (C-C-Bindung) beanspruchenden Valenzschwingung ω'_5 . Bezüglich der entarteten (e) Schwingungen des linearen Systemes mit den Frequenzen ω_3 (v) und ω_5 (dp) beachte man ferner. Wird das lineare System in die *cis*-Form deformiert, dann spaltet ω_3 auf in ω_3 (v, p) und eine Rotations-Frequenz, während ω_5 aufspaltet in ω_5 (cis, dp) und in eine nicht-ebene Schwingung ω_5 (cis, dp). Wird aber das lineare System in die *trans*-Form deformiert, dann spaltet ω_3 auf in ω'_3 (trans, v), und die nicht-ebene Schwingung ω'_3 (trans, v), während ω_5 aufspaltet in ω'_5 (trans, p) und eine Rotations-Frequenz.

VI Die ebenen Schwingungen einer verzweigten Vierer-Kette vom Typus $\begin{matrix} X \\ \diagup \\ C \cdot O \\ \diagdown \\ X \end{matrix}$. Die ebenfalls erstmalig von Lechner abgeleiteten Frequenz-Formeln findet man z. B. in S.R.E. Erg. Bd. p. 68, dort auch in Figur 8, Nr.

12 den Typus der Schwingungsformen für die drei totalsymmetrischen Schwingungen ω_1 , ω_2 , ω_3 und die zwei ebenen antisymmetrischen ω_4 , ω_5 . Berechnet wurde die Spektrale Empfindlichkeit des Systems gegen Änderungen der Federkräfte $f_{1,2}$ und $f_{1,3}$, des Winkels 2β und der Massen, m_2 . Die Ergebnisse sind in den Tabellen 5, 6, 7 und in Figur 9 zusammengestellt



$$m_2 = 16$$

$$m_1 = 12$$

$$D = 0,384 \cdot 10^5 \text{ Dyn/cm.}$$

$$d = 0,25 \cdot 10^5 \text{ ,,}$$

TABELLE V

Frequenz-Werte der ebenen Schwingungen des Modells $X \text{ CO} \cdot X$ bei Variation der federkraft $f_{1,2}$ bzw $f_{1,3}$

	$f_{1,2} = 9$	$f_{1,2} = 11$	$f_{1,2} = 13$	$f_{1,2} = 15$	$f_{1,3} = 2 \cdot 1$	$f_{1,3} = 3 \cdot 8$	$f_{1,3} = 5 \cdot 5$
ω_1	1625	1767	1900	2024	1673	1712	1758
ω_2	733	744	751	757	589	745	862
ω_3	406	407	408	408	388	402	408
ω_4		1138			882	1133	1340
ω_5		362			346	362	368

$$f_{1,2} = 3 \cdot 84 \cdot 10^5, m_2 = 15; 2\beta = 110^\circ$$

$$f_{1,2} = 10 \cdot 25 \cdot 10^5, m_2 = 15, 2\beta = 110^\circ$$

Am einfachsten liegen die Verhältnisse, wenn nur die Federkraft $f_{1,2}$ variiert wird (Tab 5), vorausgesetzt, daß sie groß bleibt gegenüber $f_{1,3}$. Die antisymmetrischen Schwingungen ω_4 , ω_5 sind aus Symmetrie-Gründen—die Feder $f_{1,3}$ darf bei ihnen nicht beansprucht werden—frequenz-unabhängig von $f_{1,2}$. Für die symmetrischen Schwingungen zeigt die Rechnung, daß die Deformations-Frequenz ω_3 fast garnicht, die Valenzfrequenz ω_2 nur sehr wenig von $f_{1,2}$ abhängt. So daß die Auswirkung einer Variation der starken Feder $f_{1,2}$ im wesentlichen die "C O-Frequenz" ω_1 betrifft, die nahezu linear mit $\sqrt{f_{1,2}}$ zunimmt. Von der Veränderung der Federkraft $f_{1,2}$ werden dagegen alle Frequenzen betroffen (Tab 5), am wenigsten ändern

sich die Deformations-frequenzen ω_3 und ω_4 , am stärksten die Valenzfrequenzen ω_2 und ω_5 , deren Quadrate wieder nahezu linear mit $f_{1,2}$ zunehmen

TABELLE VI.

Variation des Winkels 2β im Modell $X \cdot CO \cdot X$

	$2\beta = 0$	$2\beta = 60^\circ$	$2\beta = 90^\circ$	$2\beta = 100^\circ$	$2\beta = 110^\circ$	$2\beta = 120^\circ$	$2\beta = 180^\circ$
ω_1	1876	1816	1755	1734	1714	1694	1634
ω_2	861	839	811	798	785	763	711
ω_3	340	361	386	397	409	420	473
ω_4	711	974	1128	1174	1216	1253	1351
ω_5	605	450	395	376	368	357	351

$$f_{1,2} = 10,0 \cdot 10^5, f_{1,3} = 4,45 \cdot 10^5, m_3 = 15$$

Die Veränderung des Valenzwinkels 2β der CX_3 -Gruppe wirkt sich auf alle Frequenzen aus, wie Tabelle 6 zeigt und zwar am stärksten in dem praktisch wichtigen Winkel-Intervall von $2\beta = 80^\circ$ bis $2\beta = 120^\circ$, $\omega_1, \omega_2, \omega_5$ nehmen mit zunehmendem Winkel ab, ω_4 und ω_3 nehmen zu. Bei $2\beta \sim 100^\circ$ überkreuzen sich die Kurven der nicht rassengleichen Deformations-Schwingungen ω_3 und ω_4 , unterhalb 100° ist daher $\omega_3 > \omega_4$, oberhalb 100° ist es umgekehrt. Von besonderem Interesse ist es, daß die "CO-Frequenz" mit abnehmendem Winkel 2β wächst, denn es folgt z. B. daraus, daß die in den esocyclischen Ketonen Cyclohexanon \rightarrow Cyclopentanon \rightarrow Cyclobutanon beobachtete Erhöhung der CO-Frequenz von 1703 auf 1733 und 1774 mindestens zum Teil auf die mit abnehmender Ringgliederzahl eintretende Abnahme des Winkels 2β zurückzuführen ist. Aus Tabelle 6 folgt, daß ein Frequenz-Unterschied von $1755 (90^\circ) - 1714 (100^\circ) = 41 \text{ cm}^{-1}$ ($\sim 2.3\%$) in dieser Art erklärt werden kann.

TABELLE VII

Frequenz Werte und Potential Anteile der Federkräfte für die ebenen Schwingungen des Modells X CO·X bei variation der Substituenten-Masse

		$m_3 = 1$	$m_3 = 2$	$m_3 = 0.25$	$m_3 = 15$	$m_3 = 36$	$m_3 = 80$	$m_3 = \infty$
ω_1	$\omega =$	2851	2130	1754	1714	1702	1698	1695
	$v(f_{1,2})$	1.95	13.98	70.0	81.0	83.9	84.85	85.5
	$v(f_{1,3})$	97.8	84.50	23.96	14.18	11.42	10.56	9.90
	$v(D)$	0.24	1.28	3.92	3.69	3.58	3.52	3.48
	$v(d)$	0.08	0.42	1.28	1.20	1.16	1.14	1.13
ω_2	$\omega =$	1638	1519	1086	785	615	540	476
	$v(f_{1,2})$	69.8	76.7	24.8	17.6	15.48	14.88	14.52
	$v(f_{1,3})$	2.26	15.6	75.2	81.0	75.6	68.2	58.4
	$v(D)$	21.1	5.84		1.27	6.87	12.75	20.53
	$v(d)$	6.88	1.92		0.42	2.14	4.14	6.69
ω_3	$\omega =$	1269	943	579	409	287	202	
	$v(f_{1,2})$	28.1	9.52	4.20	2.21	0.76	0.21	
	$v(f_{1,3})$	0.00		0.84	4.56	13.02	21.2	31.70
	$v(D)$	54.3	68.45	71.6	70.50	65.00	59.3	50.99
	$v(d)$	17.78	22.30	23.32	22.96	21.20	19.22	17.18
ω_4	$\omega =$	2908	2163	1464	1216	1102	1055	1017
	$v(f_{1,2})$							
	$v(f_{1,3})$	99.8	99.0	95.9	91.0	86.2	83.9	82.1
	$v(D)$							
	$v(d)$	0.2	1.0	4.1	9.0	13.8	16.1	17.9
ω_5	$\omega =$	796	638	400	368	296	254	209
	$v(f_{1,2})$							
	$v(f_{1,3})$	0.1	1.0	4.1	9.2	14.0	16.2	18.0
	$v(D)$							
	$v(d)$	99.9	99.0	95.9	90.8	86.0	83.8	82.0

$m_1 = 12$, $m_2 = 16$, $2\beta = 110^\circ$, $f_{12} = 10$, $f_{13} = 4.45$, $D = 0.384$, $d = 0.25 \cdot 10^8 \text{ Dyn/cm}$.

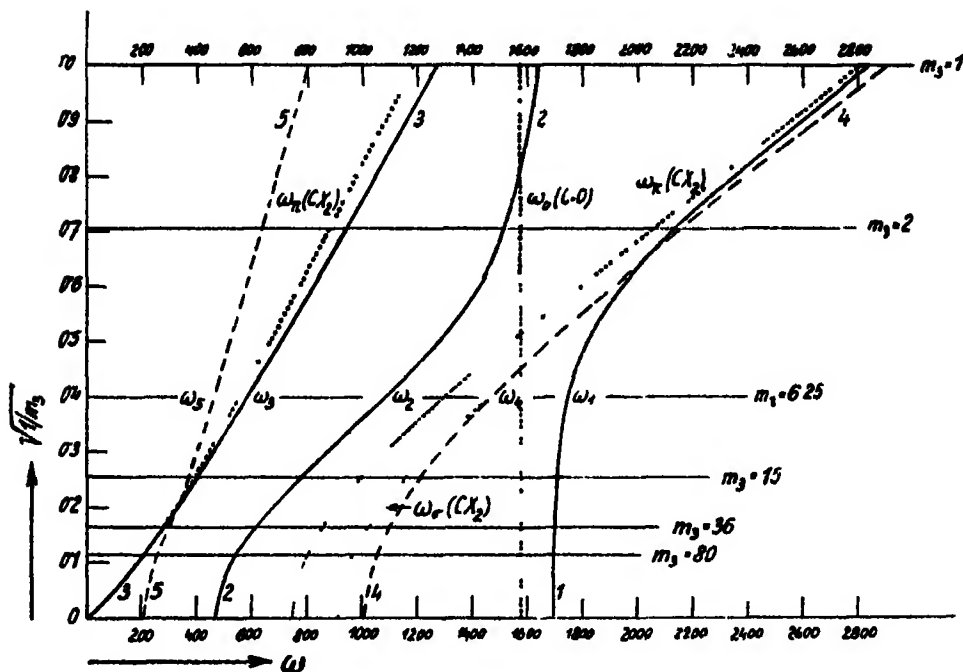


FIG. 9

Die Frequenzen der symmetrischen (ausgezogene Kurven) bzw. antisymmetrischen (gestrichelte Kurven) ebenen Schwingungen in Abhängigkeit von der Masse m_3 der Substituenten X für das Modell $X \cdot C \cdot O \cdot X$. Auf den punktierten Kurven liegen die Eigenfrequenz ω_0 ($C \cdot O$) der $C \cdot O$ Bindung, die Frequenz ω_σ (CX_2) der antisymmetrischen sowie die Frequenzen ω_π (CX_2) der symmetrischen zur Gruppe CX_2 gehörigen Schwingungen.

In Tabelle 7 und in Figur 9 ist der Frequenz-Gang bei Variation der Substituenten-Masse m_3 beschrieben. Der Vergleich der Figuren 4, 6, und 9 zeigt diesbezüglich trotz Verschiedenheit der Modelle bemerkenswerte qualitative Ähnlichkeiten, insbesondere zwischen den Modellen $X \cdot C \cdot C \cdot X$ (*trans*) und $X \cdot CO \cdot X$. Im Einzelnen sei kurz ausgeführt:

ω_1 : Für kleine m charakteristisch für die Valenzschwingung ω_π (CX_2) der Gruppe CX_2 , für große m wird ω_1 zur CO -Frequenz ω_3 . Für kleine m charakteristisch für die $C \cdot O$ -Gruppe, für große m charakteristisch für die Valenzfrequenz ω_π (CX_2), ω_1 und ω_2 vertauschen also ihre Rollen. ω_4 ist während des ganzen Kurvenverlaufes nahe oder vollkommen gleich der antisymmetrischen Gruppen-Frequenz ω_σ (CX_2). ω_3 ist charakteristisch für die symmetrische Deformations-Schwingung ω_π (CX_2) der CX_2 -Gruppe. ω_5 gehört zu einer Knick-Schwingung des Systemes $X \cdot CO \cdot X$, die beim Zusammensetzen dieses Systemes aus einer CO - und einer CX_2 -Gruppe als

funfte Schwingung (ebenso wie die hier nicht behandelte nicht-ebene Schwingung ω_6) neu hinzukommt

Das gleiche, was aus der m_3 -Empfindlichkeit der Frequenzen über ihre Zuordnung zu den System-Schwingungen abzuleiten ist, lässt sich aus den Angaben der Tabelle 7 betreffend die Energie-verteilung auf die einzelnen Form-erhaltenden System Kräfte ablesen. Bei ω_1 verschiebt sich der Hauptanteil der Energie bei zunehmender Masse m_3 von der CX_2 -Gruppe [$\nu(f_{1,3})$] nach der CO-Gruppe [$\nu(f_{1,2})$], bei ω_2 ist es umgekehrt. Bei ω_3 steckt fast die ganze Energie in der Beanspruchung der Deformations-Federn D und d, insbesondere in ersterer, die für die CX_2 -Gruppe charakteristisch ist. Bei ω_4 wird nahezu die ganze Energie auf Beanspruchung der Federn $f_{1,3}$ verbraucht, bei ω_5 dagegen für die Beanspruchung der Konstanten d, die weder dem System, C O noch dem System CX_2 , sondern erst dem Gesamtsystem X CO X angehört. Diese Angaben über Verteilung der Energie, zusammengekommen mit den Symmetrie-Eigenschaften der betreffenden Schwingungen vermitteln auch sofort eine Vorstellung über die Form der Schwingungen, so daß auf diese wohl nicht gesondert eingegangen werden muss.

Während zur "C O-Frequenz" für $m_3 = \infty$ bis $m_3 \simeq 8$ die Schwingung ω_1 und für $m_3 \simeq 2$ bis $m_3 \simeq 0,9$ die Schwingung ω_2 gehört, übernimmt für $m_3 < 0,4$ bis $m_3 = 0$ die Schwingung ω_3 die Rolle der Doppelbindungs-Frequenz, wobei der Wert $\omega_0(C O) = 1580$ approximiert wird. Man überlegt leicht auch ohne Rechnung, daß dies so sein muss. Denn wenn m_3 gegen Null geht, kann nur mehr die Eigenfrequenz ω_0 des Systems C O, das "nichts weiß" von den angehängten unendlich leichten Massen m_3 , im endlichen Frequenz-Bereich verbleiben, alle andern Frequenzen des Systems X CO X müssen unendlich werden. Da nun die C O-Frequenz jedenfalls eine symmetrische Schwingungs-Form ist und da sich die zu gleichrassigen Schwingungen gehörigen Frequenz-Kurven nicht überschneiden dürfen, so muss es die *tiefste* Frequenz des Systems X CO X sein, die beim Uebergang zu $m_3 = 0$ endlich bleibt.

Umgekehrt muss es aus den gleichen Gründen die *höchste* symmetrische Schwingung des Systems X CO X, nämlich ω_1 sein, die beim Uebergang zum andern Extrem, das ist $m_3 = \infty$ und $f_{1,3} = 0$, endlich bleibt mit dem Wert $\omega_0 = 1590$, während alle anderen System-Frequenzen Null werden.

EIGENSCHWINGUNGEN MECHANISCHER MOLEKÜLMODELLE.

IV. Der Viererring

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(Mit 4 Figuren im Text)

Es werden die durch Versuche festgestellten Schwingungsformen und Eigenschwingungszahlen von mechanischen Modellen des Cyclobutans, Cyclobutens und Cyclobutadiens sowie des Cyclobutanons und Cyclobutan-1, 3-dions mitgeteilt und mit den Forderungen der Theorie verglichen, die Übereinstimmung ist im allgemeinen befriedigend. Bei jenen Formen jedoch, die durch reine Deformation von Ringen mit gerader Gliederzahl entstehen, stellt sich ein großer Unterschied zwischen theoretisch erwarteter und experimentell beobachteter Frequenz ein; dies wird durch Zurückführung auf eine Eigenschaft des mechanischen Modelles quantitativ geklärt. Ferner wird an einem Beispiel der Einfluß des Auftretens von Drehschwingungen einzelner Massen nachgewiesen und erörtert.

Einleitung

DIE Untersuchung der Eigenschwingungen mechanischer Molekülmodelle¹,² wurde nun auch auf Modelle des Cyclobutans und seiner Abkömmlinge ausgedehnt. Die Versuchsanordnung ist gleich geblieben. Stahlmassen, die durch kräftige Schraubenfedern verbunden sind, werden auf langen Stahlstäben aufgestellt, diesem System wird über gespannte Gummischnüre durch einen Schwinghebel Energie zugeführt. Im Resonanzfall bilden sich die Eigenschwingungsformen aus, die objektiv photographisch festgehalten oder bei stroboskopischer Beleuchtung subjektiv beobachtet werden können. Die minutlichen Eigenschwingungszahlen (ω) werden an einem mit dem schwingenden Hebel gekuppelten Tachometer abgelesen. Eine Verbesserung der stroboskopischen Beobachtungsmethode wurde dadurch erzielt, dass an Stelle der lichtschwachen Glühlampen ein Neonleuchtrohr eingebaut wurde, als Spannungswandler dient ein Induktorium, bei dem der Neef'sche Hammer durch einen mit der Antriebsmaschine gekoppelten und etwas langsamer als diese laufenden Unterbrecher ersetzt wird. Diese neue Einrichtung verbessert unter anderem die objektive Demonstrationsmöglichkeit ganz wesentlich.

Cyclobutan, Cyclobuten und Cyclobutadien

§ 1 Die Schwingungsformen dieser drei Modelle sind in Fig. 1 wiedergegeben, zu ihr sowie zu den Figuren 2 und 4 ist zu bemerken, dass der

¹ Verg. F. Trenkler, *Physik Z.*, 1935, 36, 162 u. 423; 1936, 37, 338.

² A. W. Reitz, *Z. physik. Chem.*, 1937, B 35, 363.

grosseren Deutlichkeit halber die Amplituden ungefähr sechsfach vergrössert gegenüber den Modellabmessungen eingetragen sind Sowohl Richtung als Grosse der Bahnen sind aus Photographien der schwingenden Modelle ermittelt, die Pfeile an den Bahnenden lassen die Phasenunterschiede zwischen den Bewegungen der einzelnen Massen erkennen

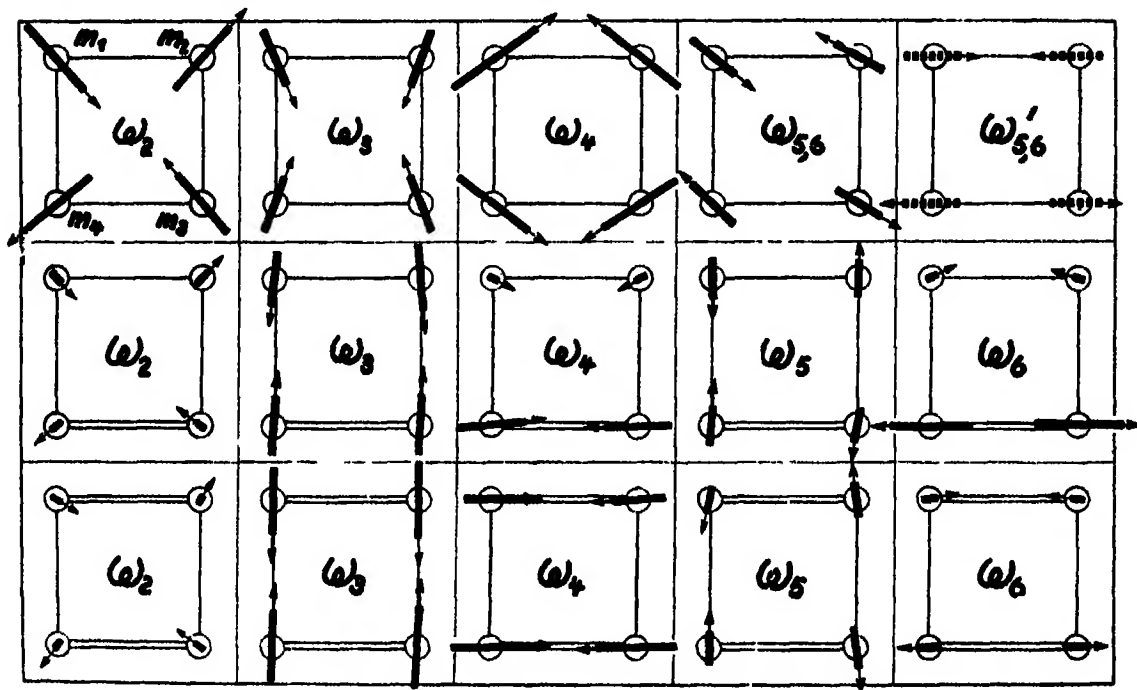


FIG 1

Schwingungsformen der Modelle von Cyclobutan, Cyclobuten und Cyclobutadien

Für den Cyclobutanring mit der Symmetrie D_{4h} (ebenes System mit vierzähliger Drehachse) sind ausser der nicht-ebenen Deformations-Schwingung ω_1 die am Modell nicht aktiviert werden kann vier ebene Schwingungsformen zu erwarten drei einfache Schwingungen ($\omega_2, \omega_3, \omega_4$) und eine zweifach entartete ($\omega_{5,6}$)³ Die am Modell beobachteten Formen entsprechen, abgesehen von kleinen Richtungsabweichungen der Bahnen, dieser Erwartung, sie werden im folgenden der Reihe nach besprochen

ω_2 ist eine "reine" Deformationsschwingung, bei der die Federn in der Längsrichtung nicht beansprucht werden Die Bahnen sind fast genau zentral gerichtet, die Amplituden aller Massen sind, ebenso wie bei den drei

³ K. W. F. Kohlrusch und R. Skrabal *Wiener Anzeiger*, 1946, Nr. 16

andern Schwingungen, erwartungsgemäss nahezu gleich gross, nämlich bei m_1 11,9, m_2 11,5, m_3 10,6 und m_4 12,3 Millimeter. Beim Uebergang zum Cyclobuten und Cyclobutadien ändern sich die Bahnrichtungen fast garnicht, dagegen werden die Amplituden auffallend kleiner (Mittelwerte. Cyclobutan 11,6, Cyclobuten 1,9 und Cyclobutadien 1,0 Millimeter), eine Erklärung für diese Abnahme fehlt. Ueber den bei dieser Form aussergewöhnlich grossen Unterschied zwischen der beobachteten und berechneten Schwingzahl vergleiche man die folgenden Abschnitte.

ω_3 und ω_4 sind zwei "reine" Valenzschwingungen, bei denen die Winkel sich nicht ändern, die totalsymmetrische Form ω_3 hat die Amplituden m_1 8,1, m_2 7,8, m_3 7,9 und m_4 8,2 Millimeter, während sie bei ω_4 für m_1 13,9, m_2 13,3, m_3 12,0 und m_4 12,1 Millimeter betragen. Die Bahnrichtungen weichen schon beim Cyclobutan merklich von den Diagonalen bezw. den zu diesen Senkrechten ab, in denen sie liegen sollten, der Grund dafür dürfte nicht in einer Unsymmetrie des Modells sondern in dem Umstand zu suchen sein, dass die beiden Formen ω_3 und ω_4 in einem reinen Valenzkraftsystem die gleiche Schwingzahl haben, d. h. "zufällig" miteinander entarten. Dementsprechend liessen sich neben dem in Fig 1 wiedergegebenen Formen ω_3 und ω_4 auch Schwingungsformen gleicher Frequenz der Art anregen, wie sie in Fig 2 dargestellt sind, sie entstehen durch Ueberlagerung von ω_3 und ω_4 mit Phasendifferenzen von ungefähr $\frac{\pi}{2}$.

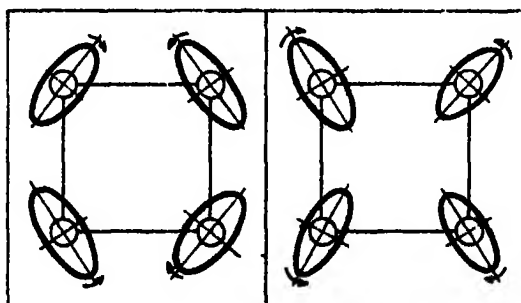


FIG 2

Zwei Formen der "zufälligen" Entartung im Cyclobutanmodell.

Setzt man dagegen die beiden Formen mit nahezu gleicher Phase zusammen dann tritt das ein, wovon die beobachteten Formen der Fig 1 bereits eine Andeutung geben: zwei sich gegenüberliegende Federn dehnen sich im Gleichtakt, während das andere Federpaar unbeansprucht bleibt. Das sind zugleich jene Schwingungsformen, die bei Cyclobuten und Cyclobutadien mehr oder weniger rein auftreten.

$\omega_{1,6}$ ist eine zweifach entartete Schwingung, die zu ihr orthogonale Form erhält man, wenn man sich das Schwingungsbild der Fig 1 um 90° gedreht denkt. Die Amplituden sind bei m_1 7,9, m_2 7,6, m_3 6,8 und m_4 8,1 Millimeter gross. Eigentlich entartete Formen mit elliptischen Kurvenbahnen konnten zwar subjektiv beobachtet, wegen geringer Stabilität jedoch nicht photographiert werden. Wurde man zwei zueinander orthogonale Normalschwingungen $\omega_{1,6}$ mit gleichgrossen Amplituden und gleicher Phase zusammensetzen, dann entstünde eine zweite entartete Normalschwingung $\omega'_{1,6}$, eine solche Form konnte zwar nicht angeregt werden, sie ist aber in Figur 1 mit gestrichelten Amplituden eingetragen, um den Zusammenhang mit den bei Cyclobuten und Cyclobutadien tatsächlich beobachteten Formen herzustellen, bei denen zwei sich gegenüber liegende Federn im Gegentakt gedehnt bzw gedrückt werden, während die zwei andern Federn in Ruhe bleiben.

§ 2 Die *Eigenschwingzahlen* erhält man aus folgenden Gleichungen-
 $\left(n = \frac{2\pi}{60} \cdot \omega = \text{Kreisfrequenz} \right)$.

<i>Cyclobuten</i>	<i>Cyclobutadien</i>	<i>Cyclobutan</i>
$n_2^2 + n_6^2 = \frac{1}{m} (f + 5d + D) + \frac{1}{M} (f + d + 5D)$	$n_2^2 = \frac{8}{M} D$	$n_2^2 = \frac{8}{m} d$
$n_2^2 \cdot n_6^2 = \left(\frac{1}{m^2} + \frac{6}{mM} + \frac{1}{M^2} \right) (fd + 4dD + fD)$	$n_2^2 = \frac{2}{M} f$	$n_2^2 = n_4^2 = \frac{2}{m} f$
$n_3^2 = f \left(\frac{1}{m} + \frac{1}{M} \right)$	$n_4^2 = \frac{2}{M} F$	$n_6^2 = \frac{2}{m} (f + 2d)$
$n_4^2 + n_6^2 = \frac{1}{m} (2f + d + D) + \frac{1}{M} (2F + d + D)$	$n_6^2 = \frac{2}{M} (f + 2D)$	
$n_1^2 \cdot n_6^2 = \frac{2}{mM} [fF + (f + F)(d + D)]$	$n_6^2 = \frac{2}{M} (F + 2D)$	

Hierin bedeuten $m = 1270$ g Masse mit zwei einfachen Federn

$M = 1342$ g Masse mit einfacher und doppelter Feder

$f = 8,84 \cdot 10^8$ dyn/cm rüchtreibende Kraft der einfachen Feder

$F = 16,00 \cdot 10^8$ dyn/cm rüchtreibende Kraft der doppelten Feder

$d = 1,56 \cdot 10^8$ dyn/cm Deformations-Konstantedes Winkels zweier einfacher Federn

$D = 1,98 \cdot 10^8$ dyn/cm Deformations-Konstante des Winkels zwischen einfacher und doppelter Feder.

In Tabelle I sind die nach obigen Formeln berechneten den am Modell beobachteten Schwingzahlen gegenüber gestellt. Die Uebereinstimmung zwischen Rechnung und Versuch ist für ω_3 bis ω_6 als hinreichend anzusehen, die Abweichungen $(\omega_{ber} - \omega_{beob})/\omega_{ber}$ sind teils positiv, teils negativ und schwanken zwischen 1 und 7%. Nur ω_2 , die Schwingzahl der reinen Deformationsschwingung, hat, wie schon beim ebenen Sechsering, einen gegen die Rechnung viel zu grossen Wert.

TABELLE I

*Berechnete und beobachtete Schwingzahlen für die Modelle
von Cyclobutan, Cyclobuten, Cyclobutadien*

		ω_2	ω_3	ω_4	ω_5	ω_6
Cyclobutan	ber	947 (1339)	1127	1127		1310
	beob	1450	1160	1100		1280
Cyclobuten	ber	1023 (1418)	1115	1208	1300 (1311)	1584
	beob	1440	1130	1220	1250	1660
Cyclobutadien	ber	1044 (1477)	1103	1485	1328	1658
	beob	1440	1130	1600	1250	1680

§ 3 *Das abnormale Verhalten der Schwingzahl ω_2 lässt sich an Hand der Fig. 3 erklären, in der die Schwingungsform ω_2 des Cyclobutanmodells unter Vernachlässigung der kleinen Richtungsabweichungen im richtigen Grossenverhältnis gezeichnet ist. Die Ruhelage ist fein eingezeichnet, die Lage der Massen und Federachsen im Umkehrpunkt stark ausgezogen. Die Form ω_2 ist zu den beiden Diagonalen m_1m_3 und m_2m_4 symmetrisch, daher kann sich keine der Massen um ihre zur Zeichenebene lotrechte Achse verdrehen, die an den Massen befestigten Federn müssen sich also in der eingetragenen s-förmigen Form krümmen. Daraus ergibt sich: Man darf für die Bestimmung der der Auslenkung einer Masse senkrecht zu ihrer Bindung widerstehenden Kraft (der "Deformationskonstanten") bei Ringsystemen mit gerader Massenzahl nicht mehr den Fall eines einseitig eingespannten und am freien Ende mit einer Kraft P belasteten Balkens ansetzen, sondern muss ausser dieser Kraft P noch ein Moment M einführen, das die durch P bewirkte Verdrehung des freien Endquerschnittes gegen den eingespannten Querschnitt wieder aufhebt.*

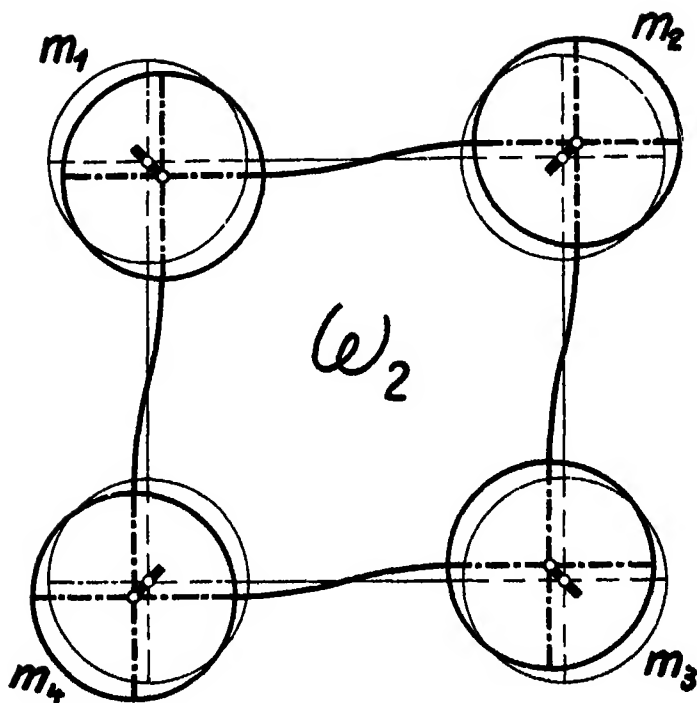


Fig. 3

Beanspruchung der Federn bei der Schwingung
des Cyclobutanmodells

Berücksichtigt man diese Forderung im Potentialansatz, so ergibt sich für n_2 des Cyclobutan- bzw. Cyclobutadienmodells

$$n_2^2 = \frac{16}{m} d \quad \text{bzw.} \quad n_2^2 = \frac{16}{M} D,$$

d. h. man hat mit dem doppelten Wert der in § 2 angegebenen Deformationskonstanten zu rechnen. Damit erhält man die in Tabelle I geklammerten Erwartungs-Werte für ω_2 , die mit den beobachteten Schwingzahlen gut übereinstimmen. Ist n_2^2 in Gleichungen höheren Grades mit anderen Frequenzquadraten gekoppelt, so ist eine nur teilweise Verdopplung des Wertes der Deformationskonstanten vorzunehmen, so lauten die Frequenzgleichungen für n_2^2 und n_3^2 des Cyclobutens nach umgeänderten Potentialansatz

$$n_1^2 + n_3^2 = \left(\frac{1}{m} + \frac{1}{M} \right) (f + d + D) + 4 \left(\frac{d'}{m} + \frac{D'}{M} \right)$$

$$n_1^2 n_3^2 = \left(\frac{1}{m^2} + \frac{6}{mM} + \frac{1}{M^2} \right) [D' (f + 2d) + d' (f + 2D)],$$

hierin sind d und D wie in § 2, d' und D' jedoch doppelt so gross einzusetzen. Setzt man $d' = d$, $D' = D$ so resultieren wieder die früher angegebenen Gleichungen. Wie die geklammerten Werte bei ω_2 und ω_5 des Cyclobutens in Tabelle I zeigen, wird ω_5 durch die Verdopplung nur unwesentlich beeinflusst, während ω_2 auf einen mit dem Versuch übereinstimmenden Wert erhöht wird.

§ 4 Drehschwingungen einzelner Massen, ihr Einfluss auf die Schwingzahl. Fig. 4 zeigt, dass bei jenen Schwingungsformen, bei denen nicht

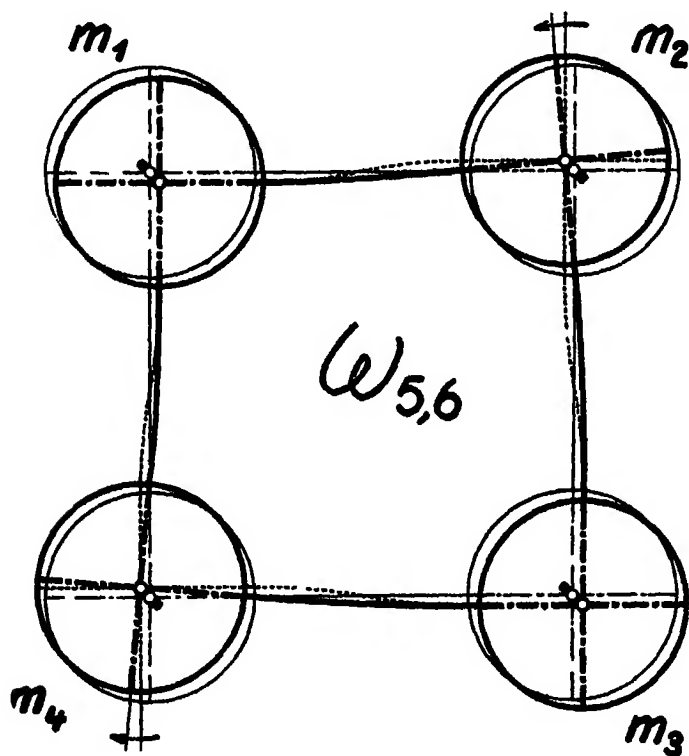


FIG. 4

Drehung der Massen bei der Schwingung
des Cyclobutanmodells

alle Bahnen in Symmetrieachsen liegen, die punktiert eingetragene s-formige Deformierung der Federn durch eine kleine Verdrehung der nicht auf den Symmetrieachsen sich bewegendenden Massen m_2 und m_4 vermieden werden kann. Dank der verbesserten stroboskopischen Beleuchtung konnte eine solche Verdrehung dieser und zwar nur dieser Massen auch in der Tat während des Schwingungsvorganges beobachtet werden. Solche Drehschwingungen

einzelner Massen innerhalb einer Systemschwingung können die Schwingzahl beeinflussen, wie ein Versuch an einem in 1, 3-Stellung durch Zusatzmassen beschwerten Cyclobutanmodell zeigte.

Dieses Modell hat einen niedrigeren Symmetriegrad (v_h) als das des Cyclobutans und daher keine notwendig entarteten Schwingungen, ω_6 und ω_8 entarten nun aber zufällig und gehorchen der Gleichung

$$n_6^2 = n_8^2 = \left(\frac{1}{m} + \frac{1}{m'} \right) (f + 2d),$$

die mit der vergrosserten Masse $m' = 1695$ g die Schwingzahl $\omega_6 = \omega_8 = 1226$ ergibt. Die beobachteten Schwingungsformen entsprechen der für Cyclobutan und $\omega_{6,8}$ in Fig 1 wiedergegebenen, nur dass jetzt bei ω_6 die unbeschwerten Massen m , bei ω_8 die beschwerten Massen m' im Gleichtakt auf der Diagonalen schwingen, im ersten Fall sind es also die schweren, im zweiten Fall die leichteren Massen, durch deren Verdrehung (vergl Fig 4) die s-formige Deformierung der Federn vermieden wird. Die Schwingzahlen werden mit $\omega_6 = 1120$ und $\omega_8 = 1150$ beobachtet, beide Werte sind infolge der Drehschwingungen zweier Massen kleiner als der Rechnungswert 1226, sie sind überdies nicht gleich gross, da bei ω_6 das Trägheitsmoment der sich drehenden Massen grosser als bei ω_8 ist. Setzt man die Zusatzmassen (die m auf m' vergrossert) nicht so wie bisher zentral sondern seitlich an, wodurch das Trägheitsmoment der Massen m' noch wesentlich starker vergrossert wird, dann sinkt ω_6 auf 960, während ω_8 mit 1160 praktisch unverändert bleibt.

Cyclobutanon und Cyclobutan-1, 3-dion

§ 5 *Die Schwingungsformen* — Von einer zu Fig 1 analogen zeichnerischen Wiedergabe der bei den beiden Modellen tatsächlich auftretenden Schwingungsformen wurde, um die Arbeit nicht mit Figuren zu überlasten, abgesehen. Am Cyclobutanon-modell wurden alle sieben, am Cyclobutan-1,3-dion-Modell nur 8 von den neun zu erwartenden ebenen Formen beobachtet, es fehlt eigenartigerweise, gerade jene Form (ω_6) die beim Cyclobutanon die grossten Elongationen aufweist. Die Uebereinstimmung mit den Forderungen der Modell-Symmetrie (vergl Fig 1 in der mechfolgenden Arbeit von Kohlrausch-Skrabal) ist im übrigen im allgemeinen befriedigend.

§ 6 *Die Eigenschwingungszahlen* — Es werden folgende Frequenzgleichungen für die ebenen Formen abgeleitet

Cyclobutanon	$\left\{ \begin{aligned} n_2^2 + n_3^2 + n_5^2 + n_6^2 &= \left(\frac{1}{m} + \frac{3}{m} \right) (f + 3d) + \left(\frac{1}{m'} + \frac{1}{m} \right) D + \left(\frac{1}{m'} + \frac{1}{M} \right) F \\ n_2^2 n_3^2 + &= \frac{2}{m} \left(\frac{1}{m'} + \frac{1}{m} \right) (f^2 + 1(fd + 8d^2) + \frac{2}{m} D \left[\frac{1}{m'} (2f + 3d) \right. \\ &\quad \left. + \frac{1}{m} (f + 3d) \right] + F \left[\left(\frac{3}{mm'} + \frac{1}{m'M} + \frac{3}{Mm} \right) (f + 3d) \right. \\ &\quad \left. + \left(\frac{1}{mm'} + \frac{1}{m'M} + \frac{1}{Mm} \right) D \right] \\ n_2^2 n_3^2 n_5^2 + &= \frac{8}{m^2} \left(\frac{1}{m} + \frac{3}{m'} \right) fd (f + 2d) + \frac{1}{m^2} \left(\frac{1}{m} + \frac{3}{m'} \right) \\ &\quad fd (f + 6d) + \frac{2}{m} F \left[\left(\frac{1}{mm'} + \frac{1}{m'M} + \frac{1}{Mm} \right) \right. \\ &\quad \left. (f^2 + 1(fd + 8d^2) + \frac{1}{m} D \left(\frac{1}{m'} + \frac{1}{M} \right) (f + 3d) \right. \\ &\quad \left. + \frac{1}{m'M} D (2f + 3d) \right] \\ n_2^2 n_3^2 n_5^2 n_6^2 &= \frac{1}{m^2} \left(\frac{1}{mm'} + \frac{3}{m'M} + \frac{1}{Mm} \right) fF [fd (f + 2d) \\ &\quad + D (f + 6d)] \end{aligned} \right.$
S (σ_x)	
as (σ_x)	
Cyclobutandion	$\left\{ \begin{aligned} n_4^2 + n_5^2 + n_6^2 &= \left(\frac{1}{m'} + \frac{3}{m} \right) (f + d) + \left(\frac{1}{m} + \frac{3}{m'} + \frac{2\sqrt{2}}{m'} + \frac{2}{M} \right) D \\ n_4^2 n_5^2 + &= \frac{2}{m} \left(\frac{1}{m} + \frac{1}{m'} \right) f (f + 2d) + 2D \left[\left(\frac{1}{m^2} + \frac{3}{mM} + \frac{1}{Mm'} \right) \right. \\ &\quad \left. + (f + d) + \frac{5 + 3\sqrt{2}}{mm'} f + \frac{4 + 2\sqrt{2}}{mm'} d \right] \\ n_4^2 n_5^2 n_6^2 &= \frac{1}{m} \left(\frac{1}{m^2} + \frac{F + 4\sqrt{2}}{mm'} + \frac{4}{m'M} + \frac{4}{Mm} \right) fD (f + 2d) \\ n_4^2 + n_5^2 + n_6^2 &= \left(\frac{1}{m'} + \frac{1}{m} \right) (f + 4d) + \left(\frac{1}{m'} + \frac{1}{m} \right) D + \left(\frac{1}{m'} + \frac{1}{M} \right) F \\ n_4^2 n_5^2 + &= \frac{16}{mm'} fd + \frac{4}{mm'} fD + F \left(\frac{1}{mm'} + \frac{1}{m'M} + \frac{1}{Mm} \right) \\ &\quad (f + 4d + D) \\ n_4^2 n_5^2 n_6^2 &= \frac{4}{mm'M} fF (4d + D) \\ n_4^2 + n_5^2 &= \left(\frac{1}{m'} + \frac{1}{m} \right) f + \left(\frac{1}{m} + \frac{3}{m'} + \frac{2\sqrt{2}}{m'} + \frac{2}{M} \right) D \\ n_4^2 n_5^2 &= 2fD \left(\frac{1}{Mm} + \frac{3}{mm'} + \frac{2\sqrt{2}}{m'M} + \frac{1}{m'M} \right) \\ n_5^2 + n_{12}^2 &= \left(\frac{1}{m'} + \frac{1}{m} \right) (f + 2d) + \left(\frac{1}{m'} + \frac{1}{m} \right) D + \left(\frac{1}{m'} + \frac{1}{m} \right) F \\ n_5^2 n_{12}^2 &= F \left(\frac{1}{mm'} + \frac{1}{m'M} + \frac{1}{Mm} \right) (f + 2d + D) \end{aligned} \right.$
S (σ_x), S (σ_y)	
as (σ_x), as (σ_y)	
S (σ_x), as (σ_y)	

$$\text{as } (\sigma_x), \text{ S } (\sigma_y) \quad \begin{cases} n_6^2 + n_{11}^2 & = \left(\frac{1}{m'} + \frac{1}{m} \right) (f + 2d) + \left(\frac{1}{m} + \frac{3}{m'} + \frac{2}{\bar{m}} + \frac{2}{\bar{M}} \right) D \\ n_0^2 + n_{11}^2 & = 2D \left(\frac{1}{m\bar{m}'} + \frac{1}{m'\bar{M}} + \frac{1}{\bar{M}\bar{m}} \right) (f + 2d) \end{cases}$$

Es bedeutet (s) symmetrisch, (a) antisymmetrisch, σ_x, σ_y sind die Symm Ebenen durch die C O-Bindungen, bezw senkrecht zu ihnen

$m = 1270$ g unbesetzte Ringmasse, $m' = 1270$ g besetzte Ringmasse,
 $\bar{M} = 1268$ g Aussenmasse,

$f = 8,84 \cdot 10^6$ dyn/cm rucktreibende Kraft der Ringfedern

$\bar{f} = 16,00 \cdot 10^6$ dyn/cm rucktreibende Kraft der Substituentenfedern

$d = 1,56 \cdot 10^6$ dyn/cm Deformations-Konstante der Winkel im Ring

$D = 1,98 \cdot 10^6$ dyn/cm Deformations-Konstante der Winkel zwischen Aussenfeder und Ringfeder

Die Gleichung vierten Grades wurde mit dem Naherungsverfahren nach Graeffe aufgelöst

Tabelle II gibt die berechneten und beobachteten Werte der Eigenschwingzahlen wieder. Abgesehen von der Deformationsfrequenz ω_2 , die wiederum beträchtlich zu hoch liegt, ergeben sich hier auch bei andern Schwingzahlen grossere Unstimmigkeiten zwischen Rechnung und Experiment. Als brauchbar kann die Übereinstimmung nur bei $\omega_4, \omega_6, \omega_9$ des Cyclobutanons und bei $\omega_5, \omega_8, \omega_{11}$ des Cyclobutandions angesehen werden. Was im Einzelnen Ursache der Unstimmigkeiten sein kann, lässt sich schwer abschätzen. Es

TABELLE II

Berechnete und beobachtete Schwingzahlen für die Modelle von Cyclobutanon und Cyclobutandion

	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8	ω_9	ω_{11}	ω_{12}
Cyclobutanon ber	797	1052	1148	1254	1546	730	1775			
beob	1340	800	1150	1220	1380	640	1870			
Cyclobutandion ber	677	1107	1209	1033	1644	915	1750	521	1798	
beob	1270	750	1170	1010	1480		1830	510	2000	

sei auf die schon beim ebenen Sechsering bezw bei seinen Abkömmlingen aufgestellten Vermutungen hingewiesen. Mangelhafte Symmetrie des Modell und Unzulänglichkeit der Anregungsvorrichtung, beides Fehler, die sich mit den vorhandenen Mitteln nicht ohne weiters beheben lassen, schliesslich ist auch ein storender Einfluss der Drehschwingungen (insbesondere bei ω_4) zu erwarten.

SCATTERING OF LIGHT IN A ROCHELLE SALT CRYSTAL *

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DEBYE's theory of specific heats of solids is based on the hypothesis of the presence of sound waves of various wave-lengths associated with the thermal energy of the medium. The existence of these elastic heat waves produces in the solid continuum stratifications in the optical density. Ignoring the molecular structure in the medium, these density fluctuations are considered responsible for the scattering of light in the medium. Many years ago, Brillouin² pointed out that monochromatic light scattered or selectively reflected by the longitudinal sound waves should exhibit a doubling which is of the nature of a Doppler effect produced by the approaching and receding wave trains. It is known, however, that in addition to the longitudinal wave, two sets of transverse wave trains should also be considered, and that these latter should also give rise to observable optical effects. The elegant experiments of Schaefer and Bergmann³ on the diffraction of light by ultrasonic waves in crystals have indeed demonstrated that for any given direction in a crystal there are in general three distinct sound velocities which generate an acoustic wave-surface of three sheets. Thus the longitudinal and the two transverse waves appearing in Debye's theory of specific heats should give rise to six Doppler Brillouin components—three on each side of the Rayleigh line. Gross⁴ has reported that he has observed the splitting up of the Rayleigh line scattered by crystalline quartz and that his observations "warrant the conclusion that the Rayleigh line of crystals appears to have six modified components." Raman and Venkateswaran¹ working with an exceptionally clear crystal of gypsum have been able to reproduce a photograph showing the six components with the main line of unaltered

* In his valedictory lecture to the Central College Physical Society on the 25th of February 1938, Sir C. V. Raman remarked that the study of light scattering in crystals should yield valuable information regarding the solid state. The present investigation which demonstrates the physical reality of the Debye heat waves in crystals is an outcome of the suggestions made in the lecture. The work now described had been completed and a paper on the same was under preparation when the note by Raman and Venkateswaran¹ on their results with a gypsum crystal appeared in *Nature* of the 8th August 1938. The author has had much pleasure in accepting the invitation to publish the results obtained by him as a contribution to this Jubilee Number in honour of Sir C. V. Raman, to whom the author is grateful for many helpful suggestions.

frequency very much suppressed in intensity Ornstein and van Cittert⁶ have pointed out that small deviations from the ideal lattice structure in crystals will scatter the Rayleigh line of unchanged frequency This line will therefore persist even in a crystal which may be visibly free from inclusions But these inclusions which it is hardly possible to avoid completely in large crystals, give rise to a lot of parasitic light in scattering experiments, thus enhancing the Rayleigh line The only crystalline solid, large and fairly clear that was readily available in this laboratory, was a Rochelle salt crystal grown by the Brush Laboratories Company and marketed by the Central Scientific Company The present paper which sets forth the results of the study of the structure of the Rayleigh lines scattered by the Rochelle salt crystal affords a definite experimental proof of the presence of the Debye waves in solids

The Rochelle salt crystal (measuring nearly 15 cm \times 8 cm \times 4 cm) was enclosed in a blackened deal wood box lined with black felt and having a horizontal slot (2 cm \times 10 cm) parallel to its longer edge in order to allow the focussing of the mercury arc light along the crystal core A circular opening of about 2 cm diameter with an ebonite tube of about 10 cm length in continuation was provided for observing the scattered light at right angles The scattered light was focussed on the slit of a spectrograph which was used in conjunction with a quartz Lummer-Gehrcke plate (20 cm long and 3.45 mm thick) for the analysis of the scattered mercury arc lines The patterns were photographed with exposures of the order of 80 hours on hypersensitive panchromatic plates These long exposures necessitate the maintenance of a constant temperature round about the high resolving power apparatus Rochelle salt crystal ($\text{K Na C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) belongs to the rhombic-hemihedral or rhombic-bisphenoidal class and possesses three diagonal axes of symmetry which coincide with the three crystallographic axes, but has no planes of symmetry The incident radiation from the mercury arc is allowed to traverse along the X-axis of the crystal, while the scattered radiation is observed along its Z-axis The surface of the Lummer plate was adjusted parallel to the Y-axis of the crystal for obtaining good resolving power, as the electric vector of the scattered radiation is mainly along the Y-axis The structure patterns of the scattered mercury arc lines λ 4358 Å and λ 5461 Å were examined and the displacements of the Doppler-Brillouin components were measured

Fig 1 gives the pattern of the scattered Rayleigh line λ 4358 Å along with the pattern of the same line directly obtained It is clear that the pattern of the scattered line contains two new components of equal intensity

which have no relation in position or intensity with the hyperfine components of λ 4358 Å. Comparing the hyperfine components with the Doppler-Brillouin components, it is readily noticed that these new components are far wider, though with the resolving power employed no structure is discernible. Assuming that the two new components observed are the Doppler-Brillouin components lying on either side of the main Rayleigh line, then wave-number separation from the main line comes out as $\pm 0.382 \text{ cm}^{-1}$. The width of each of the components is of the order 0.1 cm^{-1} , extending from $\pm 0.33 \text{ cm}^{-1}$ to $\pm 0.41 \text{ cm}^{-1}$ approximately. In spite of the fact that the wide components are not seen resolved, the width of the components must be considered as significant comprising as it probably does the components due to the transverse as well as the longitudinal sound waves in the medium. Yet another important result is the fact that the intensity total of the new components is greater than that of the main line, whose intensity has no doubt been enhanced by the parasitic light scattered by the obvious inclusions in the crystal. In spite of this source of error the intensity of the main line is much suppressed as is to be expected from theoretical considerations. Applying the Brillouin relation for the wave-number shift of the monochromatic light reflected by the thermal sound waves in the medium

$$d\nu = \pm 2\nu \frac{v}{c} \sin \frac{\theta}{2}$$

we obtain for v the value 3.53 km sec^{-1} . Judging from the width of the components the velocity range extends from about 3.0 km sec^{-1} to 3.8 km sec^{-1} . These values represent the velocities of the hypersonic sound waves (having a frequency of the order of $10^{12} - 10^{13} \sim$) in the Rochelle salt crystal mainly in a direction perpendicular to the Y-axis and at 45° with the X- and Z-axes. Since the incident light on the crystal is a convergent beam (nearly 60°) there will necessarily be a range for the angle of scattering, θ , round a mean value of 90° . This will in itself introduce a broadening in the Doppler components even if each component is sharp and single. Quite apart from this, the velocities of sound waves change with direction in the crystal. All these factors coupled with the unavoidable long exposures no doubt tend to broaden the new components and to mask their structure. No direct determination of sound velocities in Rochelle salt crystal is available for comparison with the values obtained above. The order of magnitude of the velocities can, however, be computed from a knowledge of the density (1.767 g per cc) and the elastic constants of the crystal in various directions. Mandell⁸ has determined the elastic moduli of Rochelle salt along different directions in the crystal. Calculating from those data, the velocity of compressional waves in a bar of Rochelle salt cut with its length

perpendicular to the Y-axis and at 45° with the X- and Z-axes comes out as 2.60 km sec^{-1} while the velocity along the Z-axis is 4.48 km sec^{-1} , the velocities in other directions lying within this range. The mercury green line $\lambda 5461 \text{ \AA}$ also exhibits Doppler-Brillouin components (Fig. 2), whose separations from the main line are in accord with the Brillouin formula. The components in this case appear wider due to the complications arising from the superposition of the hyperfine structure lines of Hg I $\lambda 5461 \text{ \AA}$. The main Rayleigh component is even here much less intense than the intensity total of the new components.

In conclusion, I wish to thank Prof. A. Venkat Rao Telang for his encouragement during the course of this investigation.

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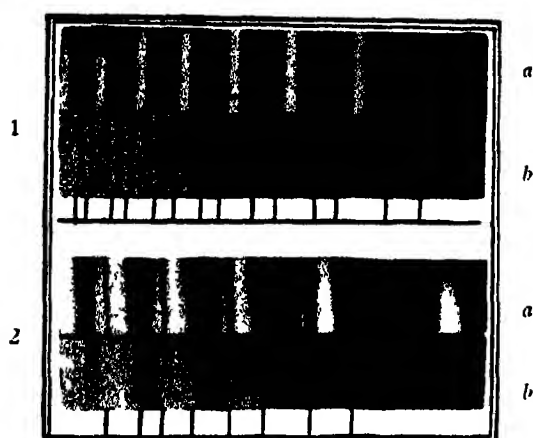


FIG. 1a—The hyperfine structure pattern of HgI λ 4358 Å in the incident spectrum
FIG 1b—The pattern of the same radiation scattered by Rochelle salt crystal
showing the Doppler-Brillouin components

FIG. 2a—The structure pattern of HgI λ 5161 Å in the incident spectrum
FIG 2b - The pattern in the scattered radiation

THE SCATTERING OF LIGHT IN SODIUM NITRATE CRYSTALS. PART I.

BY T M K NEDUNGADI

1 Introduction

THE critical study of the Raman spectra of single crystals at various temperatures and under various conditions of excitation (especially using incident polarised light) affords a prospect of leading to important advances in our knowledge of the solid state of matter. That the work done in this field is relatively small compared with the volume of published researches on substances in the liquid state is evidently due to the difficulty of obtaining crystals of satisfactory quality and size. Amongst the substances specially suitable for such work is sodium nitrate, in view of the fact that it is possible artificially to produce large transparent blocks of crystals from melts of the purified chemical. The comparatively low temperature of fusion of the substance (308°C) also enables the comparison of the effects observed in the solid and the liquid states to be readily made. Further, it is possible to cut from the prepared material, cubical blocks of crystal accurately oriented with reference to the optic axis. With such blocks it is possible to study the changes produced by varying the direction and state of polarisation of the incident light relatively to the direction of observation of the scattered light and of the crystallographic axes.

Numerous authors¹ have studied the scattering of light in sodium nitrate crystals. Amongst these, Schaeffer, Matossi and Aderhold, as also Cabannes and Canals, and Nisi have worked with single crystals. The Raman spectrum at ordinary temperature gives the following frequency shifts* —98, 189, 727, 1070, 1389 and 1669. The line 1070 is the strongest and has been identified to be ν_0 due to the symmetrical oscillation of the NO_3 ion. Lines 727 and 1389 are assigned to be ν_2 and ν_3 , the two doubly degenerate oscillations of the ion in its own plane. The weak line at 1669 may probably be an overtone of the frequency $\nu = 830$ which is due to the oscillation of the N atom along the symmetry axis of the molecule and consequently inactive in Raman effect. The two lines 98 and 189 are attributed to oscillations characteristic of the crystal lattice. Thatte and Ganesan² as also Rao³ have studied the substance in the molten condition. The former authors reported small

* The numbers in this and subsequent pages denote the wave-numbers in cm^{-1}

frequency shifts of the Raman lines when compared to those in the crystal. Aqueous solutions of the substances have also been the subject of extensive study by various authors. Recently Pattabhiramayya⁴ reported the Raman spectra of a single crystal of sodium nitrate at room temperature and at about 280° C. A perusal of his paper, however, shows that his observations are incomplete and that a more thorough and detailed investigation is called for. In the present paper are described the changes observed at a series of temperatures starting from 25 to 290° C and also when the substance is in the molten condition.

2 *Experimental Method*

The crystals were prepared in the following manner. Kahlbaum's chemical, further purified by repeated crystallisation from solution, was contained in a thin-walled glass tube. The furnace employed was a specially made one in which a steady current passing through the heating coil could establish a uniform temperature gradient down its length. The substance was melted and allowed to traverse the furnace very slowly by means of a set of gear wheels worked by means of a motor. The tapering bottom of the container facilitated the crystallisation starting at a point. The speed of the motor was so adjusted that the crystal was allowed to emerge out of the furnace in about 48 hours. The perfectly transparent block in the shape of the container so got was afterwards cut by a fine fret saw and polished to get cubes of 2 cm edge. The strong double refraction of the substance was strikingly evident with crystals cut in such a manner. The axes of the crystal were easily fixed by noting its preferred orientation in a strong magnetic field and further confirmed by examination between crossed Nicols.

The crystal, enclosed in a tightly fitting mount of oxidised copper foil, was contained in a heater (blackened inside) with suitable windows for the incident and scattered light to pass through. A thermometer with its bulb kept as near the crystal as possible served to indicate the temperature. By passing a suitable current through the heating coil, the temperature of the crystal was kept at any desired value correct to $\pm 5^\circ \text{C}$. The spectra were photographed with a Hilger two-prism spectrograph of high light gathering power and with a dispersion of about $28\text{\AA}/\text{mm}$ in the 4358 region. With a slit width of 0.04 mm, equal exposures of 30 hours were given to get the different pictures. It has been the experience of the author that the crystal if kept heated at about 290° C and exposed for a long time to mercury arc light, develops internal imperfections.

The spectrum for the molten substance was taken with the substance contained in a Wood's tube kept in a vertical position and the scattered light

reflected to the slit of the spectrograph by means of a right angled prism. The substance in this case was specially purified to avoid fluorescence. A very intense picture with absolutely no background was obtained in an exposure time of 10 hours.

The plates were carefully measured by direct comparison with a standard iron arc spectrum on a Hilger cross-slide micrometer reading correct to 1μ . The frequencies measured were correct to 2 wave-numbers.

3 Results

Very intense and clear spectrograms obtained at temperatures 25, 100, 200, 250 and 290°C and also in the molten state are reproduced in Fig. 1 of the accompanying Plate. A comparative view of the spectra at 25°C and at 290°C is afforded by Fig. 2 of the same Plate, where the pictures are taken side by side on the same photographic plate under identical conditions by the use of a Hartmann diaphragm. The frequencies of the various Raman lines measured in the spectra at 25°C , 290°C and in the molten substances are recorded in Table I. The variations in the frequencies as well as the breadths of the lattice lines at higher temperatures are given in Tables II and III. Since the frequency shifts of the fundamental oscillations of the nitrate ion at intermediate temperatures are small and within the errors of measurement, no attempt is made to tabulate them in full.

TABLE I

Exciting line $\lambda = 4358\text{ \AA}$

	ν_4	ν_5	ν_2	ν_0	ν_3	$2\nu_1$
Crystal at 25°C	98	185	720	1065	1385	1667
Crystal at 290°C	77	156	717	1061	{ 1373 to 1392	
Liquid at 320°C			713	1052	{ 1298 to 1456	

TABLE II

$$\nu = 98 \text{ cm}^{-1}$$

1 Temperature in °C	2 Centre of the line	3 $\Delta \nu$	4 Lower limit of the line	5 Upper limit of the line	6 Breadth (1 ~ 5)	7 Breadth compared to that at 25° C
25	98		94	99	5	1
100	96	2	90	101	11	2 2
200	90	8	82	97	15	3
250	85	13	71	93	22	4 4
290	77	21	62	93	31	6 2

TABLE III

$$\nu = 185 \text{ cm}^{-1}$$

1 Temperature in °C	2 Centre of the line	3 $\Delta \nu$	4 Lower limit of the line	5 Upper limit of the line	6 Breadth 4 ~ 5	7 Breadth compared to that at 25° C
25	185		180	188	8	1
100	180	5	172	189	17	2 1
200	172	13	160	187	27	3 4
250	167	18	153	188	35	4 4
290	156	29	132	178	46	5 8

The photographs show the striking changes which take place with rise of temperature. Firstly, it is of interest to note the marked increase of Rayleigh scattering at high temperatures which is to be expected theoretically. The behaviour of the low frequency lines is also remarkable. With increase of temperature, both the lines 98 and 185 broaden into bands and shift towards the exciting line in such manner that the outer edge of each band lies within the limit set by the original position of the line. The intensities of the lattice oscillations are not decreased by rise of temperature, though there is an apparent diminution which is an effect of broadening. The

observed facts are not in conformity with the report of Pattabhiramayya that the line 185 disappears at high temperatures

The spectrum for the molten substance shows a remarkably intense wing extending to about 175 wave numbers on either side of the Rayleigh line. This is significant as it shows that the appearance of lines due to lattice oscillations in the crystal and of a wing in the corresponding liquid is not a speciality with organic substances but occurs also in inorganic salts having optically anisotropic ions. The general intensity distribution in the wing for the case of molten sodium nitrate appears to be similar to that in liquids such as benzene, in the latter, as is known, the intensity of the wing is a maximum close to the incident line and falls off more or less exponentially with increasing frequency shift from it. In the crystal, on the other hand, the lattice frequency 185 at room temperature is actually of greater intensity than the 98 frequency. Due to the broadening of the lattice frequencies, the difference in the general appearance between the crystal pattern and the liquid 'wing' becomes rather less conspicuous at high temperatures. Nevertheless, it would not seem that in the crystal even near its melting point, the characteristic features of the liquid 'wing' are even roughly reproduced. It thus appears rather difficult to accept the view (due to Gross and Vuks⁶) that the wing observed in the liquid has the same physical origin as the lattice lines in the crystal.

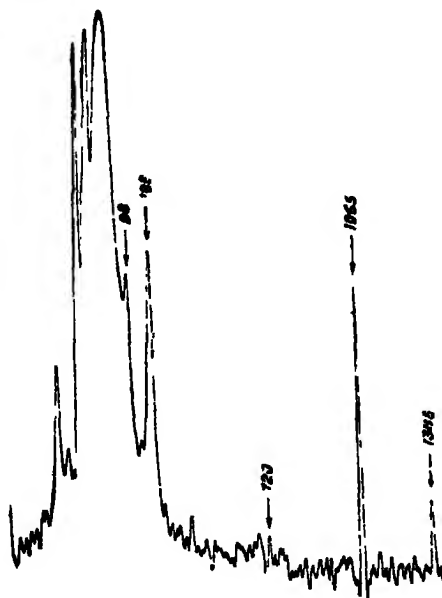


FIG. 3
Photometer curve : crystal at 25° C.

The sharp intense line 1065 becomes slightly diffuse at 290°C and a definite frequency shift of about 4 wave numbers can be detected. This shift is clearly seen in the spectra taken with the Hartmann diaphragm. In the spectrum of the molten substance, this line is still more diffuse and has decreased considerably in frequency.

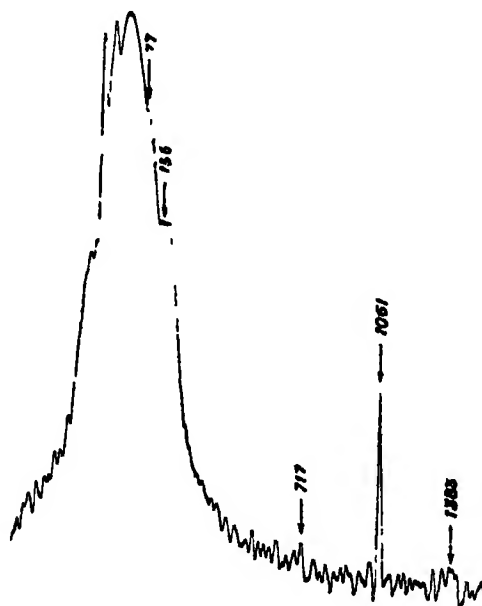


FIG 4

Photometer curve crystal at 290°C

The two degenerate oscillations 720 and 1385 also behave in a very interesting manner. At the room temperature both the lines are fairly sharp and the latter is the stronger of the two. With increasing temperature, the line 720 remains sharp whereas that at 1385 gets broader rapidly. At 290°C the first line is slightly diffuse and weaker, but in contrast to this, the line 1385 is very diffuse and broad and extends roughly to about 20 wave numbers. On account of the large broadening it is difficult to say with any degree of precision, whether there is a change in the frequency or not. A remarkable change is observed for this line in the molten substance. It becomes a broad band extending over some 160 wave numbers. The line 1667 is too faint to be measured at high temperatures. The microphotometer records (Figs 3, 4 and 5) reproduced serve to show the above effects more clearly.

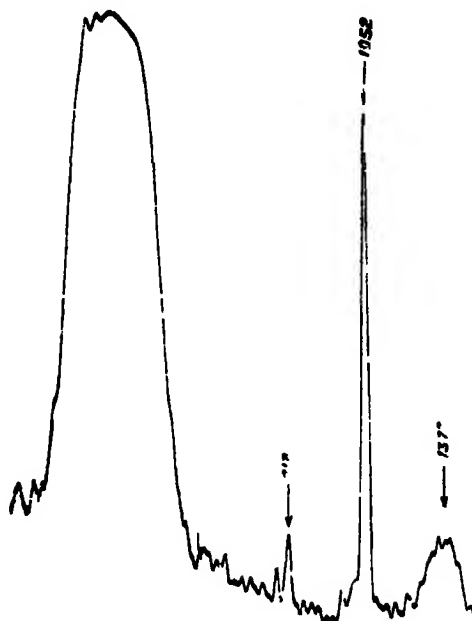


FIG. 5
Photometer curve molten state

The effect of varying the orientation of the crystal has been tried out over the whole range of temperature studied. No noticeable differences in the effects described above have, however, been found depending on the orientation, so long as the incident light is unpolarised. Using incident polarised light with various orientations of the crystal axes, very interesting results have been obtained which will be reported in a separate communication along with a theoretical discussion of the experimental results described in the present paper.

In conclusion, the author takes this opportunity to express his heartfelt gratitude to his professor Sir C. V. Raman for valuable guidance and encouragement in the course of this work. His thanks are also due to Dr. C. S. Venkateswaran for his interest in the work.

4. Summary

A detailed study of the Raman spectrum of sodium nitrate at a series of temperatures ranging from 25°C to 290°C has been carried out with fairly large single crystals prepared from melts of the substance. The investigation has also been extended to the case of the substance in the molten state. The most interesting effect noticed is the simultaneous broadening and shifting towards the exciting radiation of the lines due to

lattice oscillations with rising temperature The symmetrical oscillation of the nitrate ion shows a shift of 4 wave numbers at 290°C The 1385 line broadens out considerably as compared with the 720 line The spectrum of the molten substance shows an intense wing accompanying the Rayleigh line similar to those exhibited by aromatic liquids The 1385 line observed in the crystal becomes a broad band extending over 160 wave numbers in the molten substance

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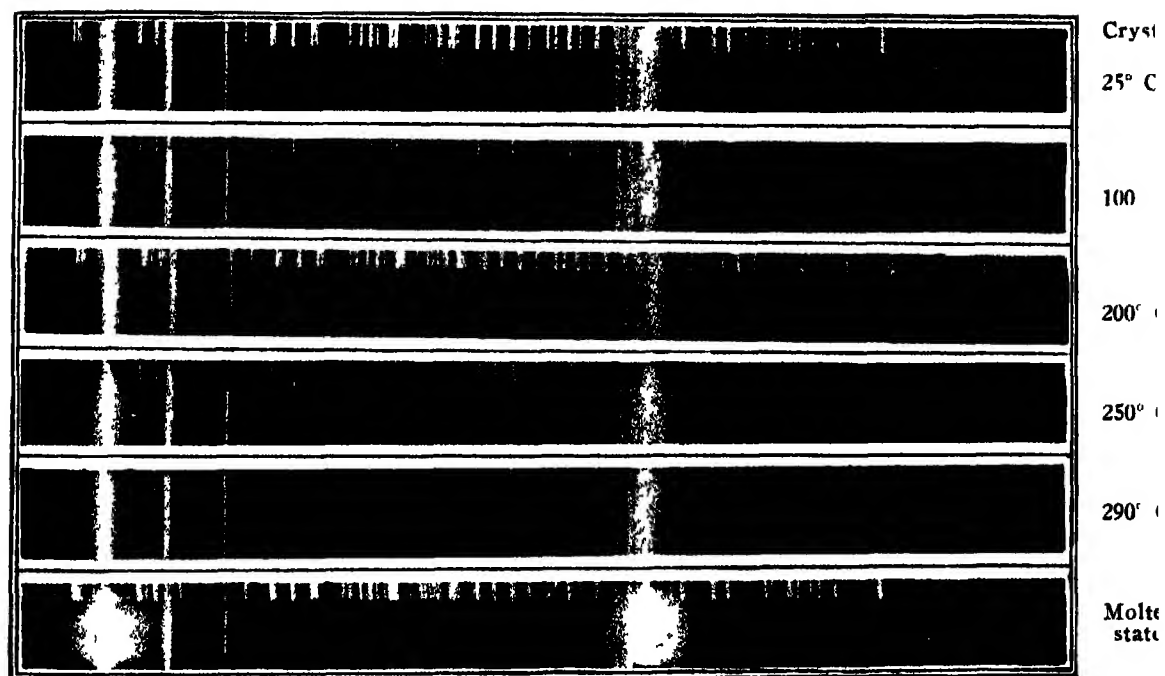


FIG 1

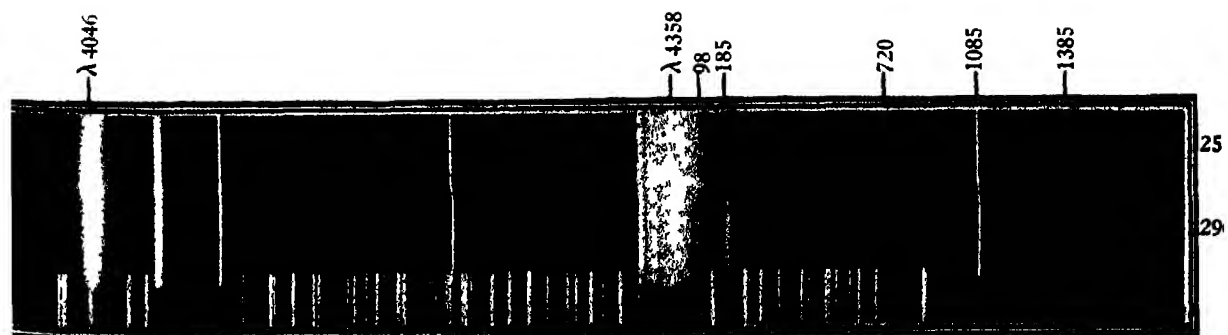


FIG 2

Raman Spectrum of Sodium Nitrate

SULLO SPETTRO RAMAN DI ALCUNI IDROCARBURI PARAFFINICI.

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GIÀ nel 1929¹ non era sfuggita ad uno di noi l'importanza che poteva presentare lo studio dell'effetto Raman degli idrocarburi specie in relazione a ricerche sui carburanti e sui petroli. Invero in tale anno si era studiato in questo laboratorio in collaborazione col Dottor Brull lo spettro Raman del pentano, eptano, ottano, decano e amilene. Molte ricerche² sullo spettro degli idrocarburi alifatici vennero poi eseguite da varie parti, in collegamento con queste, apparvero interessanti ricerche d'indole teorica sulle oscillazioni molecolari delle catene idrocarburiche³.

Il problema dello spettro Raman delle paraffine a catena normale è stato ripreso poi in modo magistrale in una nota di Kohlrausch e Koppl⁴ nel 1934. Questi autori applicando pure criteri sviluppati in precedenti lavori portano un contributo notevole sia sperimentale che teorico al problema. Si sono potute chiarire negli spettri degli idrocarburi a catene normali le oscillazioni di valenza e di deformazione rispettivamente dovute agli aggruppamenti CH [ν (CH), δ (CH)], e C—C [ν (C—C), δ (C—C)]. In questa pubblicazione i suddetti autori danno anche le righe principali delle paraffine a catena normale indicandole con le lettere *a-r*. Nelle seguenti tabella riportiamo a modo di esempio questa classificazione delle righe Raman delle catene idrocarburiche paraffiniche normali proposta da Kohlrausch e Koppl.

TABELLA I

	<i>a</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>
Pentano	334 (2 b)	837 (4)	802 (3)	898 (1)	1027 (3 b)	1070 (3 b)
Esano	318 (2 b)	820 (5 b)	865 (3)	894 (6)	1034 (3)	1075 (3)
Eptano	309 (5)	836 (3)		900 (4)	1046 (2)	1073 (3)
Ottano	281 (5)	810 (2 b)	861 (3)	889 (4 b)	1044 (3 b)	1074 (4)

Nella precedente tabella ci siamo limitati a riportare la classificazione soltanto per quelle righe che saranno oggetto di particolare discussione in

questo lavoro e che sono cioè relative ad oscillazioni di valenza e di deformazione della catena carbonica e si riferiscono a quegli idrocarburi normali per i quali è più interessante il confronto con i nostri dati sperimentali

Gli spettri delle paraffine a catena ramificata erano assai meno conosciuti ⁵

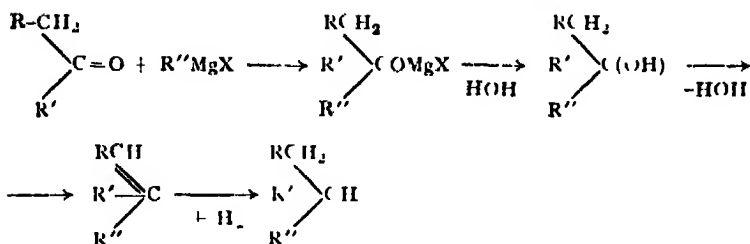
Ciò era dovuto anche al fatto della difficoltà che si ha nel procurarsi dei campioni di detti idrocarburi che sicuramente contengano un solo individuo chimico. Infatti dalla distillazione delle benzine naturali, che sono miscugli di idrocarburi capaci di dare vapori misti, non è sperabile di poter raggiungere per distillazione frazionata dei campioni di purezza conveniente

Recentemente Lecomte e Lambert⁶ hanno pubblicato un interessante lavoro dove vengono riprodotti gli spettri ultrarossi di alcuni idrocarburi a catena ramificata. Lo studio degli idrocarburi a catena ramificata isomeri dell'ottano e dell'eptano presenta uno speciale interesse perciò che riguarda le ricerche scientifiche per i carburanti. Sono note per es. le profonde differenze di comportamento (come carburante) dell'ottano normale (numero d'ottano-19) e del 2,2,4-trimetilpentano (numero di ottano 100) ⁷

Uno studio dello spettro Raman di queste sostanze avrebbe perciò anche un interesse onde approfondire eventualmente un significato scientifico dei fenomeni legati al comportamento di tali idrocarburi nei motori a scoppio

Il prof. Wibaut della Università di Amsterdam molto gentilmente ci fornì per concessione della "NV de Bataafsche Petroleum Maatschappij" una serie di idrocarburi da lui preparati per sintesi e purificati in modo speciale secondo un processo che verrà pubblicato. Questi campioni di idrocarburi paraffinici sono di una purezza superiore a quella delle migliori preparazioni che fino ad oggi sono state descritte nella letteratura. Ringraziamo perciò nel modo più vivo il Prof. J. P. Wibaut della Università di Amsterdam e la "NV de Bataafsche Petroleum Maatschappij" per questa gentile loro concessione che ci ha permesso di portare un nuovo contributo sperimentale allo studio dello spettro Raman delle paraffine proprio per quella categoria di composti che ha più spiccato interesse nel campo delle ricerche chimiche sulle benzine

Gli idrocarburi in questione erano preparati dal prof. Wibaut applicando la reazione di Grignard ai chetoni corrispondenti trasformando poi i magnesioderivati in alcoli terziari. Questi ultimi venivano disidratati e davano le olefine corrispondenti le quali, a loro volta, per idrogenazione portavano agli idrocarburi paraffinici secondo lo schema



Misure sperimentali

n Esano— D_1^{15} 0,66395, D_4^{20} 0,65943, D_4^{25} 0,65490, p e 68° , 8 a 760 mm

$\Delta \nu$ 320 (1), 366 (4), 402 (1), 496 (1), 730 (0), 830 (2), 867 (2), 895 (2), 1011 (2), 1040 (2), 1063 (2), 1076 (2), 1135 (2), 1299 (4), 1446 (4 dif), 2855 (3), 2873 (10), 2910 (8), 2936 (10), 2963 (6). Questo derivato è stato studiato anche da Okubo e Hamada (*Sci Rep Toho, Ku Univ*, 1929, **18**, 601), Petrikaln e Hochberg (*Z phys chem*, 1929, B **3**, 217), Canals Godchot e Cauquil (*C R*, 1932, **194**, 176, Andant, Lambert e Lecomte (*C R*, 1934, **198**, 1316), Kohlrausch e Koppl (*Z phys chem*, B, 1934, **26**, 209). I nostri risultati sono in ottimo accordo con quelli degli autori citati.

n Eptano— D_1^{20} 0,68378, D_4^{25} 0,67954, p e 98° , 4 a 760 mm

$\Delta \nu$ 310 (4), 397 (2), 487 (1), 839 (1), 898 (2), 1040 (2), 1082 (2), 1136 (1), 1298 (4), 1446 (6 dif), 2859 (6), 2877 (2), 2911 ($4\frac{1}{2}$), 2942 (8), 2965 (6). Questo derivato è stato anche studiato da Ganesan e Venkateswaran (*Nature*, 1929, **124**, 57), Bonino e Brull (*Gazz Chim It*, 1929, **59**, 660), S C Sirkar (*Ind J Phys*, 1932, **7**, 257), Collins (*Phys Rev*, 1932, **40**, 829), Kohlrausch, Koppl (*l c*). I nostri risultati sono in ottimo accordo con quelli degli autori citati.

2 Metilesano— D_1^{20} 0,67869, D_4^{25} 0,67437, p e 90° , 1 a 760 mm

$\Delta \nu$ 305 (4), 791 (1), 820 (4), 870 (3), 891 (4), 947 (1), 1143 (2), 1169 (1), 1299 (2), 1335 (1), 1449 (6 dif), 2870 (8), 2922 (1), 2939 (1), 2964 (6)

2,2 Dimetilpentano— D_1^{17} 0,67824, D_4^{20} 0,67388, D_4^{25} 0,66953, p e 79° , 3 a 760 mm

$\Delta \nu$ 152 (1), 175 (0), 325 (1), 345 (1), 499 (4), 747 (8), 881 (6), 924 (6), 1041 (4), 1107 (2), 1208 (4), 1245 (4), 1270 (1), 1319 (2), 1446 (6), 1459 (1), 2704 (1), 2849 (2), 2876 (8), 2910 (10), 2940 (6), 2963 (8)

3,3 Dimetilpentano— D_1^{20} 0,69330, D_4^{25} 0,68911, p e 86° , 1 a 760 mm

$\Delta \nu$ 363 (1), 413 (1), 440 (1), 487 (2), 691 (8), 793 (2), 856 (3), 910 (4), 931 (4), 948 (2), 1031 (2), 1078 (4), 1196 (3), 1232 (1), 1280 (1), 1343 (1), 1385 (1), 1445 (6 dif), 2868 (2), 2900 (8), 2946 (5), 2971 (6)

2 3 *Dimetilpentano*— D_4^{10} 0,69514, D_4^{25} 0,69087, p_e 89°, 8 a 760 mm

$\Delta \nu$ 427 (1), 464 (1), 560 (1), 713 (2), 743 (4), 748 (4), 789 ($\frac{1}{2}$), 849 (2), 916 (4), 966 (2), 985 (2), 1034 (2), 1164 (2), 1186 (1), 1284 (1), 1302 (1), 1356 (1), 1445 (6 dif), 1459 (6 dif), 2819 ($\frac{1}{2}$), 2877 (10), 2908 (3), 2939 (5), 2965 (10)

2 4 *Dimetilpentano*— D_4^{15} 0,67714, D_4^{20} 0,67275, D_4^{25} 0,66837, p_e , 80°, 6 a 760 mm

$\Delta \nu$ 149 (1), 169 ($\frac{1}{2}$), 179 ($\frac{1}{2}$), 309 (6), 469 (3), 807 (8), 869 ($\frac{1}{2}$), 918 (2), 955 (4), 985 (2), 1033 ($\frac{1}{2}$), 1160 (4 dif), 1246 (1), 1318 (2), 1341 (2), 1453 (6 dif), 2717 (1), 2843 (2), 2873 (8), 2921 (3), 2937 (3), 2963 (8)

2 2 3 *Trimetilbutano*— D_4^{10} 0,69007, D_4^{25} 0,68583, p_e , 81°, 0 a 760 mm

$\Delta \nu$ 368 (1), 393 (1), 449 ($\frac{1}{2}$), 524 (2), 687 (8), 834 (2), 918 (6), 1082 ($\frac{1}{2}$), 1213 (5 dif), 1248 (5), 1324 (5), 1437 (6 dif), 1469 (5 dif), 2711 (2), 2869 (8), 2903 (8), 2964 (10)

n Ottano— D_4^{20} 0,7028, D_4^{25} 0,69878, p_e 125°, 8

$\Delta \nu$ 148 (2), 177 (2), 283 (2), 764 ($\frac{1}{2}$), 812 (2), 852 (1), 898 (3), 1053 (2), 1076 (3), 1136 (2), 1159 ($\frac{1}{2}$), 1301 (6), 1446 (6 dif), 2731 (1), 2854 (10), 2877 (10), 2905 (8), 2942 (10), 2967 (10)

Questo derivato è stato studiato anche da Ganesan e S Venkateswaran (*J Ind Phys*, 1929, 4, 195), Bonino, Brüll (*l c*), Krishnamurti (*Ind J Phys*, 1931, 6, 543), Collins (*l c*), Kohlrausch e Koppl (*l c*), I nostri risultati sono in ottimo accordo con quelli degli autori citati

3-*Metileptano*— D_4^{10} 0,70584, D_4^{25} 0,70178, p_e 119°, 1 a 760 mm

$\Delta \nu$ [150 (1)], 172 (0), 310 (2), 490 ($\frac{1}{2}$), 760 (1), 821 (4), 898 (2), 1152 (4), 1295 (4), 1345 (1), 1446 (6 dif), 2743 (1), 2869 (8), 2909 (8), 2948 (4), 2972 (10)

2 3 *Dimetilesano*— D_4^{10} 0,71234, D_4^{25} 0,70829, p_e 115°, 8 a 760 mm

$\Delta \nu$ [151 (1)], 177 (1), 283 (1), 399 (2), 430 (1), 467 (1), 502 (1), 551 (1), 721 (2), 761 (4), 788 (2), 848 (2), 870 (2), 899 (6), 946 (2), 1003 (2), 1034 (2), 1052 (2), 1159 (4), 1188 (2), 1301 (4), 1340 (1), 1430 (6 dif), 1450 (6 dif), 2818 (1), 2860 (3), 2874 (10), 2911 (4), 2942 (4), 2967 (10)

2 5 *Dimetilesano*— D_4^{10} 0,69426, D_4^{25} 0,69015, p_e 109°, 3 a 760 mm

$\Delta \nu$ [151 (1)], 174 (1), 260 (2), 310 (2), 448 (2), 498 (1), 567 (1), 780 (2), 839 (6), 878 ($\frac{1}{2}$), 953 (4), 1046 ($\frac{1}{2}$), 1148 (4), 1170 (4), 1223 (1), 1299 ($\frac{1}{2}$), 1333 (6),

1365 (1), 1449 (6 dif), 2718 (1), 2765 (1), 2819 (1), 2852 (4), 2870 (10), 2935 (4), 2965 (10)

Questo derivato è stato studiato anche da J Murray (*J Chem Phys*, 1934, 2, 618) I nostri dati sono in pieno accordo con quelli dell'autore citato

3 4 *Dimetilesano*— D_4^{20} 0,71951, D_4^{25} 0,71548, p_e 117°, 9 a 760 mm

$\Delta \nu$ [147 ($\frac{1}{2}$)], 171 ($\frac{1}{2}$), 339 (2), 433 (4), 562 (1), 703 (1), 730 (1), 748 (4), 794 (2), 836 (2), 896 (4), 953 ($\frac{1}{2}$), 981 (4), 1034 (4), 1046 (4), 1159 (4), 1279 ($1\frac{1}{2}$), 1353 (1), 1373 (1), 1450 (6 dif), 2731 (1), 2825 (1), 2863 (10), 2877 (10), 2913 (1), 2938 (8), 2967 (10)

Questo derivato è stato anche studiato da J Murray (*l c*) I nostri risultati sono in pieno accordo con quelli dell'autore citato, non abbiamo potuto però rilevare la riga registrata da Murray a 1658 cm^{-1}

3 *Metil-3 Etilpentano*— D_4^{20} 0,72742, D_4^{25} 0,72358, p_e 118°, 4 a 760 mm

$\Delta \nu$ 360 (1), 388 ($\frac{1}{2}$), 422 (1), 682 (8), 878 (5), 958 (3), 982 (3), 1016 (4), 1032 (4), 1084 (6), 1184 (2 dif), 1274 (1), 1336 (1), 1374 (1), 1449 (6 dif), 2734 (1), 2860 (4), 2885 (6), 2917 (6), 2944 (6), 2969 (10)

2 2 3 *Trimetilpentano*— D_4^{20} 0,71613, D_4^{25} 0,71212, p_e 110°, 1 a 760 mm

$\Delta \nu$ [151 (1)], 170 ($\frac{1}{2}$), 352 (2), 392 (2), 462 ($\frac{1}{2}$), 487 ($\frac{1}{2}$), 530 (6), 717 (8), 829 (2), 891 (4), 925 (6), 952 (4), 972 (3), 1028 (4), 1082 (3), 1115 (1), 1185, (2 dif), 1219 ($\frac{1}{2}$), 1243 (2), 1301 ($\frac{1}{2}$), 1337 ($\frac{1}{2}$), 1444 (6 dif), 1461 (6 dif), 2733 (1), 2869 (3), 2909 (8), 2948 (4), 2972 (10)

2 2 4 *Trimetilpentano*— D_4^{20} 0,69196, D_4^{25} 0,68786, p_e 99°, 1 a 760 mm

$\Delta \nu$ 150 (2), 302 (2), 426 (1), 514 (2), 747 (5), 830 (1), 901 (8), 928 (6), 1099 (2), 1168 (1), 1202 (2), 1245 (4), 1283 (1), 1344 (1), 1449 (6 dif), 2713 ($\frac{1}{2}$), 2872 (8), 2911 (8), 2944 (2), 2965 (10)

Questo derivato è stato anche studiato da Rank e Bodner (*J Chem Phys*, 1935, 3, 248) I nostri risultati sono in pieno accordo con quelli dell'autore citato.

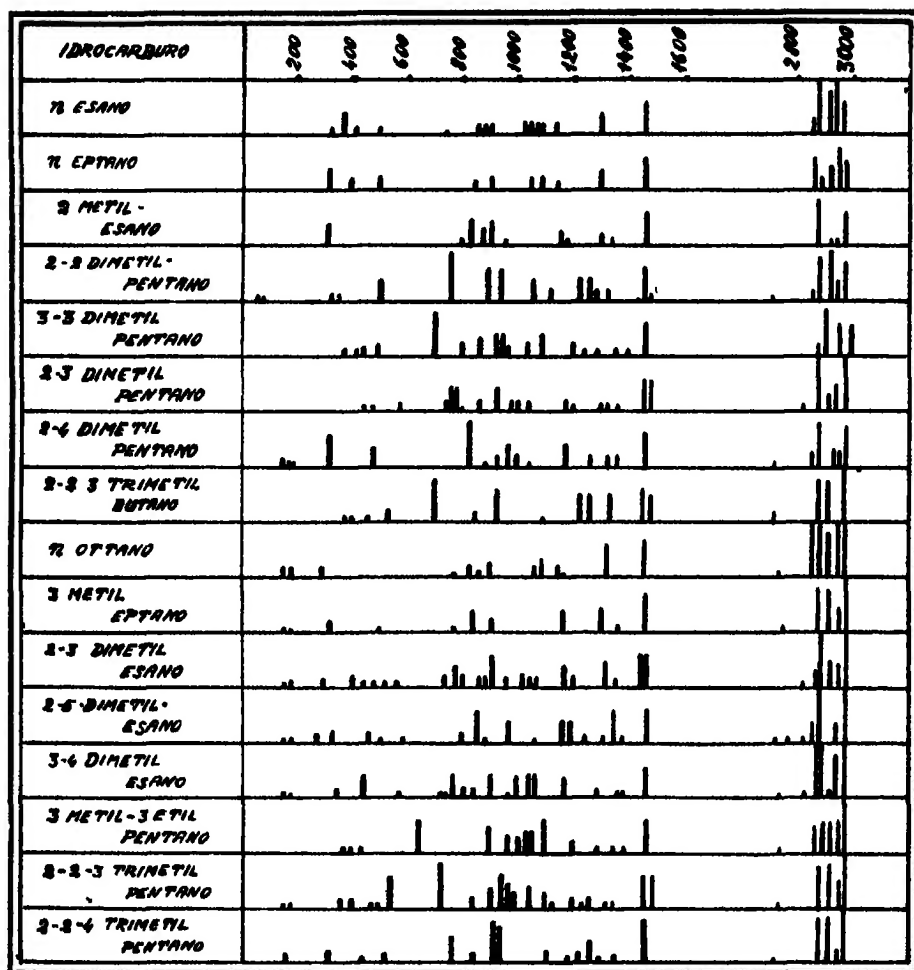


FIG 1

Discussione dei risultati

Una osservazione anche sommaria delle tabelle sperimentali e della loro riproduzione grafica riportata nella figura 1 mette in evidenza come gli spettri Raman delle paraffine a catena ramificata si differenzino nettamente da quelli dei corrispondenti idrocarburi a catena normale e ciò specialmente nella zona fra 600 e 800 cm^{-1} . Mentre negli spettri degli idrocarburi paraffinici a catena normale in questa zona mancano del tutto righe Raman o vi appaiono assai deboli, negali spettri delle paraffine a molecola ramificata abbiamo delle righe che per alcuni idrocarburi raggiungono anche notevolissime intensità.

Così nella zona tra 900 e 1000 cm^{-1} gli idrocarburi a catena ramificata mostrano righe di notevole intensità mentre nella stessa zona gli idrocarburi a catena normale non presentano alcunchè di interessante

Ricordo che la zona dello spettro Raman fra 600 ed 800 cm^{-1} è spostata rispetto alla riga *c* della classificazione a cui abbiamo accennato (vedi tabella I), verso le minori frequenze mentre la zona fra 900 e 1000 cm^{-1} è spostata verso le maggiori frequenze rispetto alla riga *e*. In ambedue queste zone per gli idrocarburi a catena normale mancano righe degne di nota

Nella zona della riga *a* si osservano negli spettri degli idrocarburi a catena ramificata dei fatti degni di rilievo. La riga *a* degli idrocarburi normali corrisponde ad una oscillazione di deformazione della catena carbonica e negli idrocarburi a catena normale varia quasi regolarmente diminuendo la propria frequenza con l'aumentare della lunghezza d'onda

TABELLA II

	<i>a</i>	<i>a'</i> $a < a' < 380 \text{ cm}^{-1}$	<i>a''</i> 380-400 cm^{-1}	<i>a'''</i> 440-450 cm^{-1}	<i>a''''</i> 470-500 cm^{-1}
<i>n</i> Eptano	309 (4)				487 (2)
2 Metilesano	305 (4)				
2 4 Dimetilpentano	309 (6)				469 (1)
2 2 Dimetilpentano		325 (1) 345 (1)			499 (4)
3 3 Dimetilpentano		363 (1)		413 (1) 440 (1)	487 (2)
2 2 3 Trimetilbutano		368 (1)	393 (1)	449 ($\frac{1}{2}$)	
<i>n</i> Ottano	283 (2)				
3 Metileptano		310 (2)			490 ($\frac{1}{2}$)
2 5 Dimetilesano	260 (2)	310 (2)		448 (2)	498 (1)
2 3 „ „	283 (1)		399 (2)	430 (1)	467 (1) 502 (1)
3 4 „ „		339 (2)		433 (4)	
3 Metil 3 etilpentano		360 (1)	388 ($\frac{1}{2}$)	422 (1)	
2 2 4 Trimetilpentano		302 (2)		426 (1)	
2 2 3 Trimetilpentano		352 (2)	392 (2)		462 ($\frac{1}{2}$) 487 ($\frac{1}{2}$)
<i>n</i> Pentano	334 (2)		399 (6)		463 (1)
<i>n</i> Butano	319 ($\frac{1}{2}$)			426 (5)	

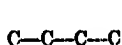
Negli eptani a catena ramificata che noi abbiamo studiato (vedi tabella 2) la detta riga *a* si mantiene nella posizione dell'eptano normale soltanto per

il 2 metilesano e per il 2 4 dimetilpentano Per gli altri eptani isomeri la riga a manca in questa posizione e si ritrovano invece gruppi di righe di minore intensità tra 320 e 500 cm^{-1} , righe che mancavano del tutto nell'eptano normale, nel 2 metilesano e nel 2 4 dimetilpentano

Un fatto analogo accade per gli ottani a catena ramificata Solo il 2 5 dimetilesano e il 2 3 dimetilesano presentano la riga caratteristica a dell'ottano normale (283 cm^{-1}) Gli altri ottani isomeri mancano di righe tra 1 200 e 300 cm^{-1} Tutti però presentano gruppi di righe tra 300 e 500 cm^{-1} , zona dove l'ottano normale non mostra alcuna riga Raman

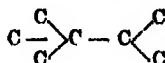
Abbiamo perciò divisa la zona tra 250–500 cm^{-1} in cinque parti che indichiamo con a , a' , a'' , a''' , a'''' La zona a' comprende righe che potrebbero corrispondere alla riga a in catene normali a minor numero di atomi di carbonio Per es il 2 2 dimetilpentano presenta una riga a' a 325 cm^{-1} che è assai vicina alla riga a $\omega = 319 \text{ cm}^{-1}$ del butano e a quella $\omega = 334 \text{ cm}^{-1}$ del pentano Così il 3 metil 3 etilpentano presenta una riga a' a 360 cm^{-1} che è vicina alla riga corrispondente del propano a 375 cm^{-1} ecc È interessante a tale proposito riprodurre lo spostamento della riga a dal butano all'isobutano paragonando poi quest'ultimo con il propano ed osservare in conseguenza l'analogia variazione fra n eptano e il 2 2 3 trimetilbutano

n butano 320 cm^{-1} Isobutano 370 cm^{-1} Propano 375 cm^{-1}



normale eptano 309 cm^{-1}

2 2 3 Trimetilbutano 368 cm^{-1}



Lo spostamento della riga a verso le maggiori frequenze nelle catene paraffiniche ramificate sembra essere tanto più sensibile quanto più i radicali alchilici sostituiti agli idrogeni nella catena principali occupano posizioni tra loro vicine tendendo ad una maggiore "centralizzazione" dello scheletro carbonico della molecola

L'osservazione della tabella (Tabella 3) ci riconferma che lo spostamento medio delle righe verso le maggiori frequenze procede non soltanto con la ramificazione della catena, ma, a parità di ramificazione, con la cosiddetta "centralizzazione" della catena carbonica Riproduciamo nella seguente tabella il valore medio della frequenza Raman nella detta zona fra 250 e 450 cm^{-1} per alcuni idrocarburi studiati:

TABELLA III

Eptano	309 cm ⁻¹	C C C C C C C
2 2 Dimetilpentano	335 „	$\begin{array}{c} \text{C} \\ \\ \text{C} \text{ C} \text{ C} \text{ C} \text{ C} \\ \\ \text{C} \end{array}$
3 3 Dimetilpentano	408 „	$\begin{array}{c} \text{C} \\ \\ \text{C} \text{ C} \text{ C} \text{ C} \text{ C} \\ \\ \text{C} \end{array}$
n Ottano	283 „	C C C C C C C C
3 Metileptano	310	$\begin{array}{c} \text{C} \\ \\ \text{C} \text{ C} \text{ C} \text{ C} \text{ C} \text{ C} \end{array}$
2 5 Dimetileptano	339 „	$\begin{array}{c} \text{C} \qquad \text{C} \\ \qquad \\ \text{C} \text{ C} \text{ C} \text{ C} \text{ C} \text{ C} \end{array}$
2 3 Dimetileptano	371 „	$\begin{array}{c} \text{C} \text{ C} \\ \quad \\ \text{C} \text{ C} \text{ C} \text{ C} \text{ C} \text{ C} \end{array}$
3 4 Dimetileptano	386 „	$\begin{array}{c} \text{C} \text{ C} \\ \quad \\ \text{C} \text{ C} \text{ C} \text{ C} \text{ C} \text{ C} \end{array}$

E' noto (come è stato anche recentemente rilevato in un lavoro di Lovell e Campbell⁷) che a parità di altre condizioni il potere antidetonante di una paraffina aumenta con la "centralizzazione" della catena carbonica nel senso sovrariferito e cioè col ravvicinamento degli alchili sostituiti in posizione sempre più simmetriche verso il centro della molecola

Così per es. nei dimetilpentani il 3 3 dimetilpentano a catena più centralizzata ha un numero di ottano 98 mentre il 2 2 dimetilpentano a catena meno centralizzata ha un numero di ottano di 5 unità inferiore al precedente. Anzi altre misure attribuirebbero al 2 2 dimetilpentano un numero di ottano di 18 unità inferiore a quello del 3 3 derivato (8)

Il gruppo di righe *c*, *d*, *e*, *f*, *g*, è da riferire con tutta probabilità ad oscillazioni di valenza della catena carbonica della molecola idrocarburica. Negli idrocarburi a catena normale le posizioni di queste righe sono praticamente costanti e si può dire indipendenti dalla lunghezza della catena, viceversa in questa parte dello spettro Raman tra 600 e 1100 cm⁻¹ la ramificazione della catena porta delle profonde variazioni

Negli idrocarburi a catena ramificata ordinariamente la riga *c* manca ovvero si può supporre che sia spostata verso le più basse frequenze dato che invece di essa si trovano una o più righe intense spostate anche di 100-150 cm⁻¹ verso le minori frequenze rispetto alle normali posizione della riga *c* che è di circa 820-840 cm⁻¹. Per gli idrocarburi studiati si può osservare che la presenza di righe intense in questa zona sotto agli 820 cm⁻¹ è indice sicuro di ramificazione della catena. Altro fatto portato dalla ramificazione consiste in una intensificazione di queste righe anche se più o meno spostate

pal la posizione normale della riga *c*. Analogamente agli spettri degli idrocarburi a catena ramificata, la riga *e*, che nelle catene normali si trova ordinariamente a 880–890 cm^{-1} , raggiunge una assai più forte intensità e si sposta verso le maggiori frequenze anche di 50–70 cm^{-1} così (vedi tabella N° 4)

TABELLA IV

	<i>c</i>		<i>c</i>	<i>d</i>	<i>e</i>	<i>e'</i>	<i>f</i>	<i>g</i>
	600–700	700–800						
Esano		730 (0)	830 (2)	807 (2)	805 (2)		1011 (2) 1040 (2)	1063 (2) 1076 (2)
Eptano			839 (1)		809 (2)		1040 (2)	1082 (2)
2 Metil-esano		791 (1)	820 (4)	870 (3)	801 (4)	947 (1)		
2,2 Dimetilpentano		747 (8)			881 (6)	924 (6)	1041 (4)	
3,3	691 (8)	791 (2)		856 (3)		910 (4) 931 (4) 948 (2)	1031 (2)	1078 (4)
2,3 Dimetilpentano		713 (2) 743 (4) 748 (4) 780 (1)		849 (2)		916 (4) 966 (2) 985 (2)	1034 (2)	
2,4 Dimetilpentano			807 (8)	869 ($\frac{1}{2}$)		918 (2) 955 (4) 995 (2)	1033 ($\frac{1}{2}$)	
2,2,3 Trimetilbutano	687 (8)		834 (3)			918 (6)		1082 ($\frac{1}{2}$)
n Ottano		704 ($\frac{1}{2}$)	812 (2)	872 (1)	808 (3)		1053 (2)	1076 (3)
3 Metileptano		760 (1)	821 (4)		809 (2)			
2,3 Dimetilecano		721 (2) 761 (4) 788 (2)		848 (2) 870 (2)	809 (6)	946 (2)	1003 (2) 1034 (2) 1052 (2)	
2,5 Dimetilecano		780 (2)	830 (0)	878 (1)		953 (4)	1046 (1)	
3,4 Dimetilecano		703 (2) 730 (1) 748 (4) 794 (2)	836 (2)		890 (1)	953 ($\frac{1}{2}$) 981 (4)	1034 (4) 1046 (4)	
3 Met 3 etilpentano	682 (8)			878 (5)		958 (3) 982 (3)	1016 (4) 1032 (4)	1084 (1)
2,2,3 Trimetilpentano		717 (8)	829 (2)		891 (4)	925 (6) 952 (4) 972 (3)	1028 (4)	1082 (3)
2,2,4 Trimetilpentano		747 (5)	830 (1)			901 (8) 929 (6)		1099 (2)

mentre nell'eptano normale la riga *e* si trova a 898 cm^{-1} nel 3,3-dimetilpentano si sposta raddoppiandosi rispettivamente a 910 e 931 cm^{-1} con intensità "4", mostrando inoltre una altra riga a 948 cm^{-1} . In altri casi come nel 2,2-dimetilpentano permane una riga in posizione *e* ordinaria (891 cm^{-1}) con intensità assai più forte che non nello spettro dell'idrocarburo normale corrispondente, ma appare una nuova riga (947 cm^{-1}) assai spostata verso le maggiori frequenze. Negli idrocarburi ramificati a 7 e 8 atomi di carbonio queste righe *e* spostate verso le maggiori frequenze possono essere anche doppie o triple.

La presenza dunque di righe intense tra 900 e 1000 cm^{-1} costituisce pure una caratteristica degli spettri delle paraffine a catena ramificata da noi studiati.

Se si considera che anche la riga *e*, come la riga *c*, sono attribuite da Kohlrausch e Koppl nel loro studio su idrocarburi normali ad oscillazioni di valenza della catena carbonica si deve concludere che il passaggio dalle catene normali a quelle ramificate porta una forte perturbazione nelle oscillazioni di valenza delle catene carboniche non solo per ciò che riguarda la posizione delle righe Raman ma anche per ciò che si riferisce alla loro intensità. In altre parole la ramificazione della catena fa risentire i suoi effetti sulla deformabilità dell'elissoide delle refrattività⁹ riferibile al complesso dei legami C-C che costituiscono lo scheletro della molecola idrocarburea.

E' noto che le ricerche tecniche hanno messo in evidenza per questi idrocarburi a 7 e 8 atomi di carbonio una differenza che caratterizza nettamente le catene normali da quelle ramificate trovando un alto indice di ottano per le catene ramificate ed un bassissimo indice per quelle normali.

Stiamo studiando appunto la possibilità di poter valutare, se pure in via di prima approssimazione, l'ordine di grandezza del numero di ottano di una miscela carburante (ben si intende senza aggiunte di antidetonanti) in base al suo spettro Raman. In via di primissimo orientamento abbiamo trovato che la radice quadrata della somma dei quadrati delle intensità delle righe Raman tra 600 e 1000 cm^{-1} segue in modo interessante l'andamento degli indici di ottano degli idrocarburi studiati. Nella Figura 2 è riportato questo andamento che noi riteniamo per ora del tutto qualitativo e provvisorio in attesa di analizzare in modo più accurato questa eventuale relazione. Per ora le intensità delle righe corrispondono ad apprezzamenti grossolani. Una determinazione microfotometrica delle intensità stesse potrà permettere una più decisiva discussione. Abbiamo in corso ricerche in proposito.

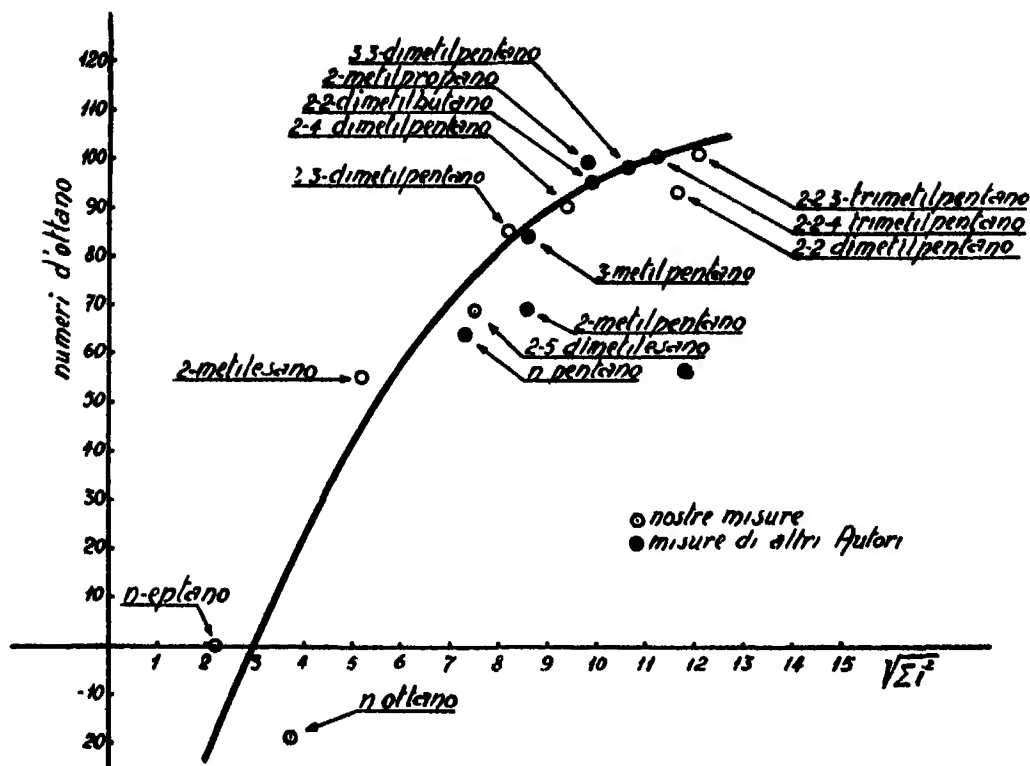


FIG. 2

Nella zona tra $1000\text{--}1100\text{ cm}^{-1}$ le righe *f* e *g* non presentano nel loro insieme gran che di caratteristico, salvo la tendenza ad uno sdoppiamento in qualche idrocarburo a catena fortemente ramificata

Resterebbero da discutere ancora le zone dello spettro Raman di questi idrocarburi tra 1100 e 1400 cm^{-1} dove cadono righe riferibili ad oscillazioni di deformazione dei legami C-H tra 1400 e 1500 cm^{-1} con le righe caratteristiche dei gruppi CH_3 oltre alla zona $2800\text{--}3000\text{ cm}^{-1}$ dove si osservano le righe corrispondenti alle oscillazioni di valenza dei gruppi C-H, CH_2 , CH_3 .

Tra 1200 e 1400 cm^{-1} il *n* esano, *n* eptano, *n* ottano mostrano una intensa riga verso il 1300 cm^{-1} . Negli idrocarburi ramificati al posto di queste righe si trovano più righe sparse in tutta l'estensione del tratto $1200\text{--}1400\text{ cm}^{-1}$. Le righe intense a $1400\text{--}1500\text{ cm}^{-1}$ non mostrano variazioni sensibili con le caratteristiche costitutive della catena carbonica.

Così pure l'insieme delle righe dovute ad oscillazioni di valenza CH tra 2800 e 3000 cm^{-1} non mostrano a prima vista caratteristiche ben nette onde differenziare per idrocarburi a 6, 7 ed 8 atomi di carbonio le catene ramificate dalle corrispondenti normali.

Concludendo l'interesse maggiore presentato dallo spettro Raman nello studio degli idrocarburi paraffinici a 6, 7, 8 atomi di carbonio a catena normale e ramificata oltrechè nella zona $250-400\text{ cm}^{-1}$ si accentua nel tratto $600-1000\text{ cm}^{-1}$ dove effettivamente le particolarità della catena carbonica presentano delle variazioni ben nette nella posizione e nella intensità delle righe Raman tanto da poter incoraggiare l'applicazione di questo mezzo di ricerca anche allo studio tecnico degli idrocarburi paraffinici

Un altro lato interessante della questione potrebbe emergere dal paragone tra gli spettri Raman e gli spettri ultrarossi. Il materiale sperimentale che si ha però a disposizione nello spettro ultrarosso è quanto mai ridotto. Recentemente Lecomte e Lamberte¹⁰ hanno dato alcuni spettri ultrarossi di paraffine lavorando su campioni di sicura identità chimica. Una difficoltà per potere accettare altri dati della bibliografia come per es. quelli di Coblenz sta appunto nella provenienza dei campioni studiati. Trattandosi in quest'ultimo caso di idrocarburi preparati per distillazione frazionata da petroli naturali manca ogni sicurezza di identificazione chimica.

Una trattazione completa d'altra parte dei rapporti tra spettro Raman e spettro ultrarosso non riesce facile per il fatto che richiederebbe la conoscenza degli spettri ultrarossi degli idrocarburi allo stato di vapore mentre le misure che noi possediamo si riferiscono quasi esclusivamente allo stato liquido. Restano perciò delle incertezze sulla applicazione delle regole di selezione.

Desideriamo ad ogni modo notare che gli spettri ultrarossi pubblicati da Lecomte e Lambert mostrano delle frequenti non coincidenze fra bande ultrarosse e righe Raman. Specialmente nella zona attorno ai $700-800\text{ cm}^{-1}$ si trova spesso una forte banda ultrarossa che manca del tutto in effetto Raman. Già Kohlrusch e Koppl nel loro lavoro hanno affrontato il problema della corrispondenza degli spettri Raman ed ultrarossi delle catene paraffiniche normali in base alle caratteristiche di simmetria. Le difficoltà già forti che si hanno nell'interpretare i caratteri di simmetria delle catene idrocarburiche normali si accentuano ancora più passando alle catene ramificate. Riteniamo perciò di dover rimandare una discussione di questo tipo a quando potremo possedere una serie più numerosa di dati sullo spettro ultrarosso dati che siamo in via di procurarci con esperienze in corso in questo Laboratorio.

A conclusione generale del nostro lavoro dato che questo avrà l'onore di essere inserito in un volume giubilare che si stampa in occasione del 50 mo anno di W. Raman teniamo a rilevare che anche dopo più di due lustri dalla scoperta di questo insigne scienziato l'effetto Raman si presenta per la chimica come un mezzo d'indagine del più alto interesse.

Si può dire che questi due lustri passati dalla scoperta di Raman siano serviti a porre delle basi poderose alle applicazioni chimiche dello spettro

Raman e che per i progressi della chimica dei decenni che verranno dovremo sempre più essere riconoscenti a questo grande scienziato che ha scoperto un metodo d'indagine fra i più sottili e potenti della chimica moderna

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A CHART OF THE RAMAN BANDS OF WATER IN CRYSTALS.

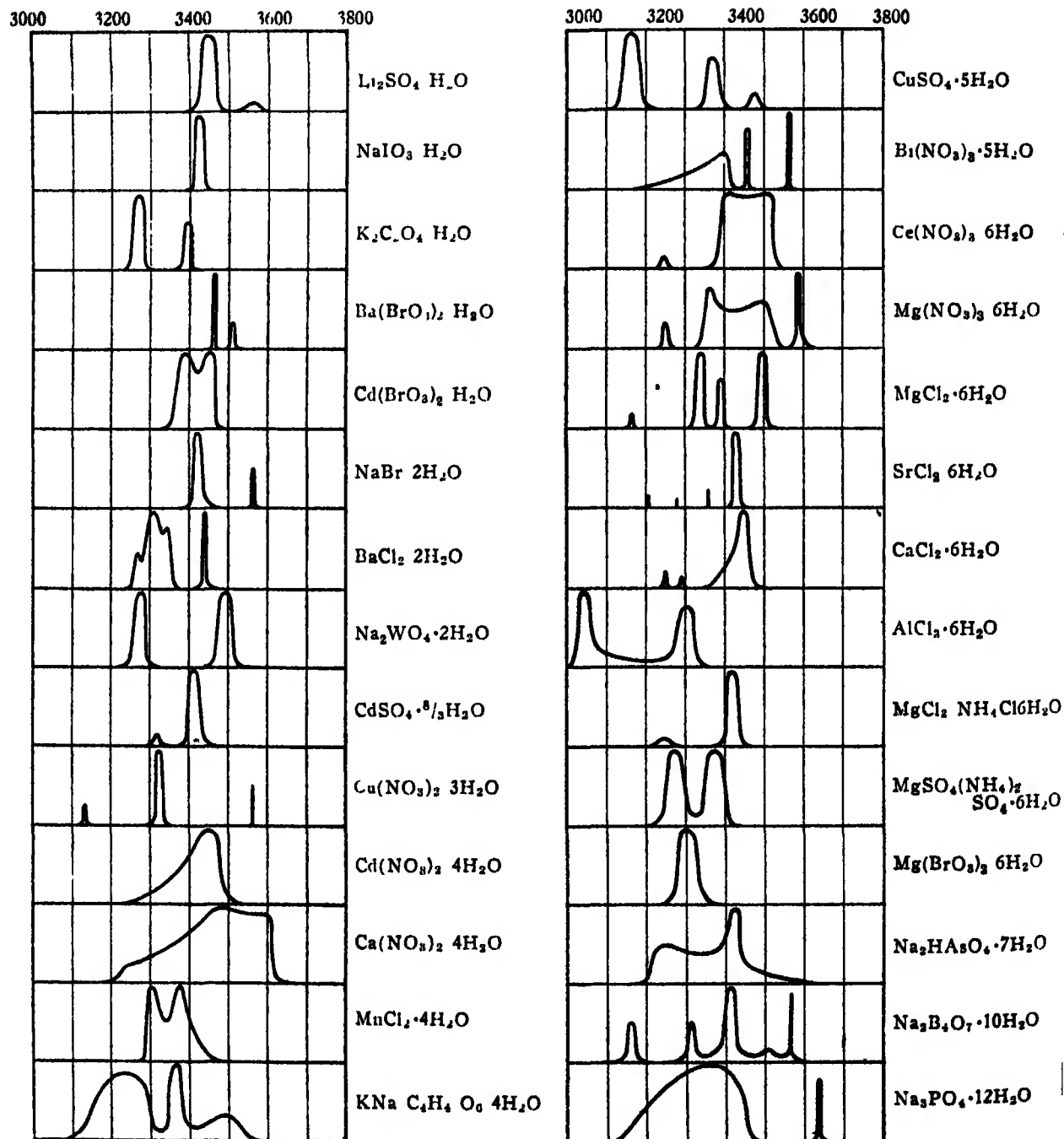
BY P G N NAYAR

1 *Introduction*

It is well known that the Raman spectrum of water in the vapour state exhibits a single line at 3654 wave-numbers, while in the liquid state the same is a very diffuse band which covers a frequency range from 3100 to 3700. In the solid state, ice at 0° shows a comparatively sharp band at 3150 followed by two fainter components at 3270 and 3390. The intensity distribution in the water band, and the influence of temperature and the presence of electrolytes on the same, have been the subject of extensive investigations for an account of which the reader may be referred to reviews by Magat (1936) and by Hibben (1933, 1937). Special mention may be made of a recent comprehensive paper by Cross, Burnham and Leighton (1937) in which theoretical explanation of the results has been attempted on the basis of the Bernal-Fowler theory of the structure of water.

It is important to remark that the Raman bands due to the bound water in crystals present a very extensive field for study. The great majority of salts when they crystallise out of water carry a definite number of water molecules as part of the crystal lattice. During the investigation of various salts, attention has also been given to the bands due to water of crystallisation, and the frequencies observed will be found listed under the various substances in the Landolt-Bornstein Tables (1935). However, a thorough study of this problem has remained difficult, as it was not possible to record the details of these faint bands except in the favourable cases of large single crystals. The difficulty has been overcome by Ananthakrishnan (1937) who drew attention to the fact that by using the technique of complementary filters described by him, it is possible to get the complete spectral details of the water bands even with crystal powders. He also studied 14 different inorganic salts and showed that the spectrum of crystal water differs widely from crystal to crystal.

In the present work, the study has been extended to 16 other substances, several of those chosen having a relatively small number of water molecules in the chemical formula. In almost every case where a substance has been



Raman Bands of Water of Crystallisation.

reinvestigated by the improved technique it has been found that the data available from old work are far from complete. The substances studied by Ananthakrishnan and those by the author taken together furnish 30 different cases in which the data are believed to be complete. It is therefore thought worthwhile at this stage to present the results to serve as a basis for theoretical discussions.

The results are collected together here in diagrammatic form to show at a glance the wide variation in the spectra with different crystals. The substances are arranged in the order of the number of water molecules in the chemical formula. Ananthakrishnan's plates were available for inspection and the diagram is based on measurements of the edges and intensity maxima of the bands. The curves have been made to represent as nearly as possible the appearance of the bands. The intensities have been estimated visually relative to the strongest component in each case, and no comparison can be made between the intensities in different cases.

Recently Canals and Peyrot (1938) have employed the same technique for the study of water bands, and given their results in the form of a chart which may be referred to for 7 additional cases.

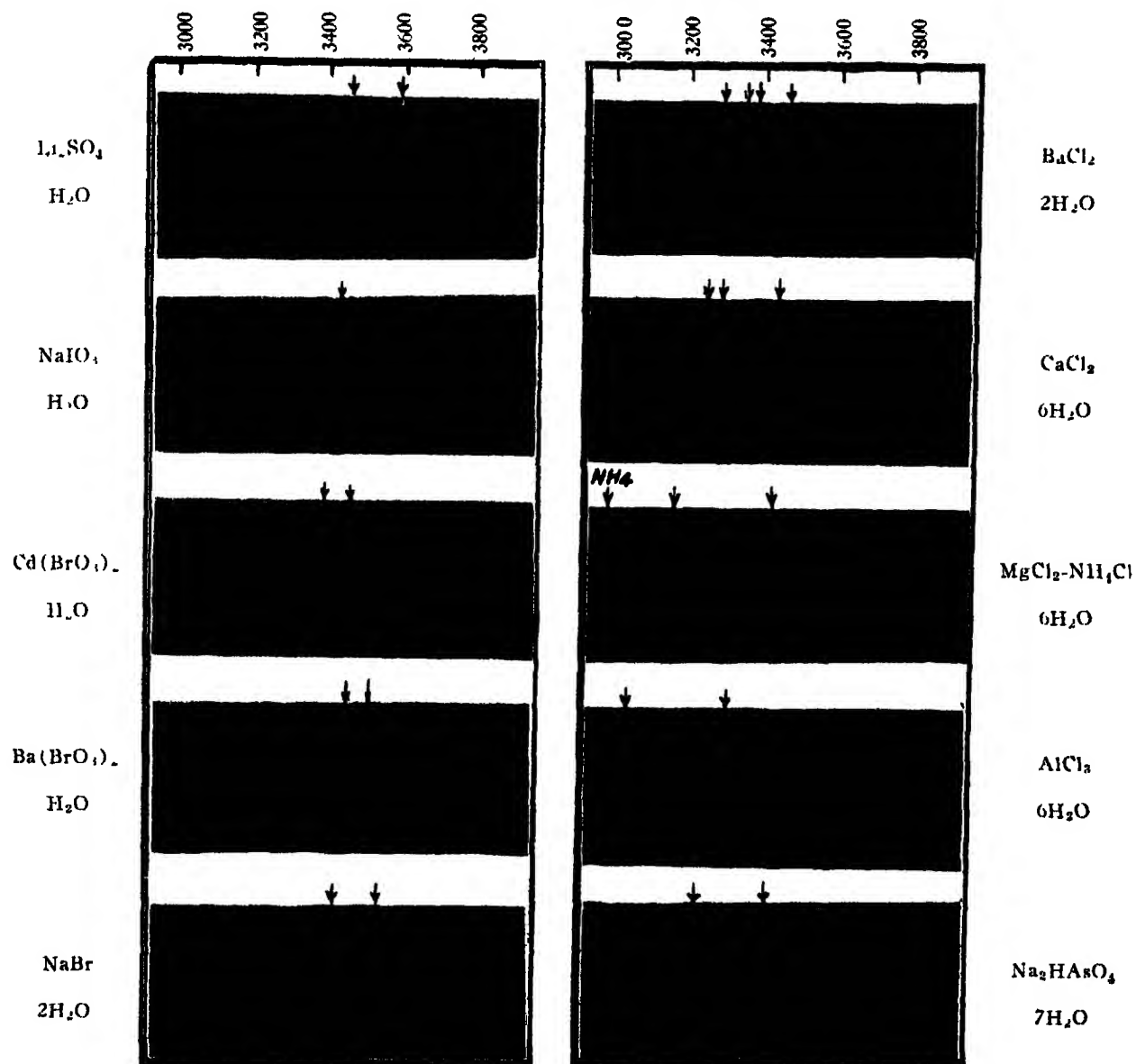
2 Experimental Arrangement and Results

The substances used were either Kahlbaum's pure chemicals or prepared by the usual methods and purified by recrystallisation. The experimental arrangement was generally the same as that described by Ananthakrishnan. In the case of substances which were liable to lose water of crystallisation by the heating caused by the mercury arc, provision was made to surround the substance with a water jacket.

The frequencies of the water bands in the substances now studied are tabulated below.

No	Substance	Frequencies of intensity maxima in cm^{-1} Intensities given in brackets with the strongest component = 10	Remarks
1	$\text{La}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	3457 (10), 3580 (1)	Diffuse bands
2	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$	3430 (10)	Band of breadth 30 wave numbers
3	$\text{Cd}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	3394 (10), 3466 (10)	Incompletely resolved doublet band
4	$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	3460 (10), 3510 (3)	Fairly sharp lines
5	$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	3275 (10), 3400 (6)	Diffuse bands
6	$\text{NaBr} \cdot 2\text{H}_2\text{O}$	3430 (10), 3570 (5)	The band of 3430 shift has a sharp edge on the short wave length side and shades off on the long wave length side. The 3570 frequency is a line
7	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	3280 (4), 3320 (10), 3360 (7), 3450 (10)	3450 is a broad line
8	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	3290 (10), 3500 (10)	Faint diffuse bands
9	$\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$	3340 (1), 3430 (10)	
10	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	3250 (8), 3394 (10), 3500 (4)	Very diffuse band extending from 3126 to 3500 with intensity maxima at the places shown
11	$\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$	3310 (10)	Diffuse band extending over 80 wave numbers
12	$\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$	3257 (1), 3430 (10)	Band at 3430 extends over 60 wave numbers. Bands observed at 2848, 3024 and 3117 have been assigned to NH_4 vibrations
13	$\text{MgSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	3284 (10), 3394 (10)	Bands observed at 2848, 3070 and 3192 assigned to NH_4 vibrations
14	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	3250 (2), 3298 (1), 3440 (10)	Main component very strong and seen visually. Excitation by 4077 also present
15	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	3044 (10); 3312 (8)	3044 is the lowest water frequency observed in any crystal
16	$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$	3250 (5), 3440 (10)	Diffuse band extending from 3224 to 3580 with a maximum at 3250 and a line superposed at 3440. A very faint band at 2975 has been assigned as due to O-H frequency of the substance itself.

Structure of Water Bands in Crystals



3 Acknowledgement

The author's thanks are due to Professor Sir C. V. Raman for his kind and encouraging interest in this work.

4 Summary

A study of the Raman bands due to water of crystallisation in 16 different substances has been made, and the results are presented along with the earlier data available from the work of Ananthakrishnan in the form of a chart

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STUDIEN ZUM RAMAN-EFFEKT.

Mitteilung XCII Das Ramanspektrum des dimeren Ketens.

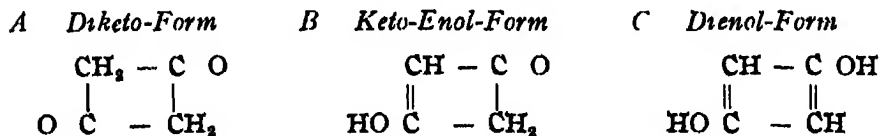
VON K W F KOHLRAUSCH UND R SKRABAL

(179, *Mitteilung aus dem physikalischen Institut der Technischen Hochschule Graz*)

Es wird das Ramanspektrum des dimeren Ketens, das in der Diketoform einem Cyclobutan-1, 3-dion entspricht, aufgenommen und zusammen mit den Spektren von Cyclobutan (-Radical) und Cyclobutanon mit den für diese drei Körper abgeleiteten Erwartungs-Spektren verglichen. Es wird festgestellt, daß der von englischen Autoren aus Dipolmoment- und andern physikalischen Messungen gezogene Schluss, das dimere Keten habe vorwiegend die Struktur der Mono-Enol-Form, mit dem Ramanspektrum unvereinbar ist. Versuche, das stabilisierte 1, 3-Dion in Form des 2, 2-4, 4-Tetramethyl-cyclobutan-1, 3-dion aufzunehmen, gaben kein gesichertes Resultat.

I Einleitung

Angus-Leckie-Le Fèvre-Le Fèvre-Wassermann¹ (abgekürzt A L F F W) haben schon vor drei Jahren die Konstitution des dimeren Ketens ($\text{H}_2\text{C}=\text{C}=\text{O}$)₂ diskutiert und dabei die folgenden Formulierungen in Betracht gezogen



Aus dem Dipolmoment, das in Benzol-Lösung zu 3,14, in Tetrachlor-Kohlenstoff-Lösung zu 3,30 gemessen wurde, folgern A L F F W, dass die Form A, die

ebenso, wie dies bei Tetramethyl-Cyclobutan-1, 3-dion $\text{O} = \text{C} \begin{array}{c} \diagup \text{C}(\text{CH}_3)_2 \\ \diagdown \text{C}(\text{CH}_3)_2 \end{array} = \text{C} = \text{O}$ festgestellt wurde, kein Dipolmoment aufweisen sollte, unmöglich allein vorliegen könne. Da weiters die Form C aus thermochemischen Messungen — die Bildungs-Wärme 1081 Kcal/Mol sei nur mit A oder B vereinbar — abzulehnen sei, müsse, die Substanz zum überwiegenden Teil die Mono-Enol-Form B besitzen, eine Folgerung, die auch mit den Daten für die Molrefraktion in Uebereinstimmung stünde. Dass es dabei gestattet ist, aus dem in Lösung gemessenen Dipolmoment Schlüsse auf die Normal-Form des Molekules zu ziehen, wurde durch die Gleichheit der Raman-Spektren für die homogene und für die in CCl_4 geloste Substanz erwiesen.

¹ W R Angus, A. H Leckie, C G Le Fèvre, R J. W. Le Fèvre und A Wassermann, *Journ chem Soc., London* 1935, 1751

Auch wir mussten uns im Laufe unserer Untersuchungen über Cyclobutan-Derivate einerseits, über gespannte esocyclische Ketone andererseits, für das Raman-Spektrum von Cyclobutan-1,3-dion, das ist die Diketoform des dimeren ketens, interessieren. Beim Studium des von A I, F F W mitgeteilten Spektrums kamen wir nun zu dem Ergebnis, dass nach allen vorliegenden Erfahrungen der Aufbau des Schwingungs-Spektrums *unvereinbar* sei mit der aus andern physikalischen Messungen gezogenen Folgerung, dass die Substanz vorwiegend die Struktur B besitze. Angesichts dieses offenkundigen Widerspruches beschlossen wir zunächst eine Neubestimmung des Raman-Spektrums, um uns durch eigene Versuche gesicherte Grundlagen für eine Diskussion des Problems vom Standpunkt des Molekülspektroskopikers zu verschaffen.

II Das Raman-Spektrum des dimeren Ketens

Die Substanz wurde aus Keten—hergestellt aus Aceton mit der Wolfram-Lampe—das einmal durch Polymerisation in Aceton (K_{p34} 49–50°), das anderemal durch Polymerisation des in der Bombe verflüssigten Ketens (K_{p37} 43–45°, F_p -12°) gewonnen. Beide Präparate gaben praktisch identische Spektren. Das in Tabelle I wiedergegebene Streuspektrum wurde aus 4 Aufnahmen, zu denen die geschätzten Intensitäten I_1 bis I_4 gehören, gemittelt. I_1 auf Platte Nr 2073, ohne Filter, 3 maliger Wechsel, Expositionszeit $t = 9$, Untergrund mittel, Spektrum stark, I_2 auf Pl 2062, mit Filter, kein Wechsel, $t = 14$, Ugd m, Sp m, I_3 auf Pl 2069, m f, $t = 14$, 2 maliger Wechsel, Ugd s, Sp st., I_4 auf Pl 2072, 7 maliger Wechsel, $t = 14$, Ugd s, Sp st.

Das aus dem Streuspektrum der Tab I abgeleitete Raman-Spektrum ist in Tab 2 den von A I, F F W mitgeteilten Ergebnissen gegenübergestellt. Dazu ist zu bemerken. Linie Nr 6 dürfte nicht reell sein, sie tritt als Streulinie Nr 26 in Tab 1 auf und ist als f-668 zu deuten. Für die Linie Nr 19 haben wir nur auf einer einzigen Platte eine recht unsichere Andeutung gefunden. Bei den Linien Nr 2, 3, 5 ist eine ausserhalb der üblichen Fehlergrenzen liegende Abweichung in den Zahlenwerten, bei den Linien Nr 20 bis 23 ausgesprochene Nicht-Uebereinstimmung festzustellen. Diesbezüglich teilte Herr Wassermann² auf eine briefliche Anfrage unsererseits Folgendes mit: "Im Gebiet 1950 waren die Linien recht breit und verwaschen, ausserdem wurde die Ausmessung gerade in diesem Gebiet auch dadurch erschwert, weil besonders viele Hg-Linien mit den Raman-Linien zusammenfielen. Ich halte es daher für möglich, dass die Differenzen 35

² Wir danken auch hier Herrn Wassermann für seine freundlichen Schreiben, die auch in anderer Hinsicht manche für uns nützliche Hinweise enthielten.

TABELLE I

Das Streuspektrum des dimeren Ketens $(H_2C \text{ C} : O)_2$ abgeleitet aus
4 Aufnahmen den relativen Linien-Intensitäten I_1 bis I_4 ,
 I_1 o F, I_2 , I_3 , I_4 m F

No	ν'	I_1	I_2	I_3	I_4	Zuordnung	No	ν'	I_1	I_2	I_3	I_4	Zuordnung
1	24553	0				k-152	26	22327	0	0	0	00	668
2	24425	4b				q-2963	27	22283	3				Schatten ? ↓
3	24387	2				p-2906 (k)	28	22268	12	5 b	8	7	e-670
4	24306	3				q-3022	29	22138	$\frac{1}{2}$	0	0	00	e-800
5	24262	4 b				k-443	30	22092	2		1	$\frac{1}{2}$	e-846
						q-3126	31	22074	3	1	1	$\frac{1}{2}$	e-864
6	24223	0				p-3130	32	21990	$\frac{1}{2}$		0	00	e 948
7	24174	1				q-3214	33	21958	3	$\frac{1}{2}$	2	1	e-980
8	24030	5 b				k-675	34	21926	1	0	1	0	e-1012
9	23892	00				k-813 (?)	35	21838	$\frac{1}{2}$	0	1	$\frac{1}{2}$	e-1100
10	23862	$\frac{1}{2}$				k-843	36	21743	10b				k 2962
11	23842	2				k-863 (i)	37	21690	10b				k-3015
12	23751	00				k-854	38	21626	$\frac{1}{2}$			00	e-1312 (f ?)
13	23717	2				k-968	39	21567	9ab	2	3	3	e-1371
14	23685	00				k-1020							k-3138
15	23607	1				k-1098	40	21493	1				k-3212
16	23521	00				i-995 (*)	41	21398	0				i-3118 ?
17	23391	00				k-1314 (?)	42	21252	3 b	0	1	1	e-1686 ± 9
18	23330	3				k-1375	43	21154	00				'
19	23085	3		0	1	e + 147	44	21082	4	0	2	2	e-1856
20	22789	7		4	4 b	e 149	45	21047	3	0	1	1	e-1891
21	22614	3	00	1	1	e-324	46	19974	3	1	0	1	e-2964
22	22500	00		00		f-435	47	19919	2				e-3019
23	22497	5	2	3	3	e-441	48	17995	0			1	e-313
24	22437	1		1	$\frac{1}{2}$	e-501	49	17871	3	2	3	3	e-437
25	22415	5	2	3	3	e-523	50	17792	4	3	4	4	e-516

TABLELLE II.

*Das Raman Spektrum des dimeren Ketens I nach Angus-Leckie-LeFèvre
Wassermann, II nach Kohlrausch-Skrabal*

No	I	II	No	I	II	No	I	II
1		140 (4)	10	865 (1)	864 (2)	19	1547 ($\frac{1}{2}$)	
2	334 (1)	324 (2)	11		951 (0)	20	1721 ($\frac{1}{2}$)	1686 (1b)
3	450 (2)	438 (3)	12	984 (1)	984 (2)	21		1856 (3)
4		501 (1)	13		1016 (1)	22	1888 (2)	1891 (2)
5	532 (2)	523 (3)	14	1104 (2)	1099 (1)	23	1933 (3)	
6	613 ($\frac{1}{2}$)		15	1185 ($\frac{1}{2}$)		24	2002 (3)	2066 (10b)
7	674 (8)	671 (8)	16	1270 ($\frac{1}{2}$)		25	3019 (3)	3010 (10b)
8		800 (0)	17		1313 (00)	26	3127 (1)	3131 (4b)
9		844 (1)	18	1374 (3)	1373 (3)	27		3213 (1)

(= 1721–1686), 32 (= 1888–1856), 42 (= 1933–1891) zum grossen Teil mit Fehlern zusammenhangen, die wir bei der Ausmessung der Platten begangen haben "

Auch bei uns sind die Linien 1686, 1856, 1891 mehr oder weniger breit und verwaschen, trotzdem würden wir den Fehler in unsern Zahlenangaben nicht höher als $\pm 5 \text{ cm}^{-1}$ einschätzen und können so grosse Unterschiede wie 32, 35, 42 cm^{-1} nicht recht verstehen Immerhin kann nach den obigen Mitteilungen Herrn Wassermann's weiter kein Gewicht auf diese Diskrepanz gelegt werden

III Diskussion des Schwingungs-Spektrums von Cyclobutan-1,3-dion

Es entspricht dem Leitgedanken unserer Untersuchungen, wenn wir das dimere keten zunächst als ein Cyclobutan-dion (Diketo-Form A) auffassen und versuchen, ob ein spektraler Anschluss an Cyclobutan bzw Cyclobutanon zu vollziehen ist

(a) Die Auswahlregeln und die Zuordnung der Schwingungs-Formen zu den einzelnen Symmetrie-Klassen sind für Cyclobutan-1,3-dion und Cyclobutanon in Tabelle 3 angegeben, die schematisierten Schwingungsformen in Figur 1

TABELLE III

Auswahlregeln und Klassifizierung der Schwingungs-Formen

	C_4^2 σ_x σ_y σ_z	Cyclobutan, D_{4h}				
A_{1g}	S S S S	p $1a$	ω_8	δ_1 ν_1		
A_{1u}	S aa aa aa	v $1a$		γ_2		
A_{2g}	S aa a^2 S	v $1a$		γ_1		
A_{2u}	S S S aa	v M_2		δ_2 ν_2		
B_{1g}	aa S S S	dp $1a$	ω_2	δ_1 ν_1		
B_{1u}	aa aa aa aa	v $1a$		γ_2		
B_{2g}	aa aa aa S	dp $1a$	ω_4	γ_1		
B_{2u}	aa S S aa	v $1a$	ω_1	δ_2 ν_2		
B_{2g}	C C C aa	dp $1a$		γ_2 δ_2 ν_2		
E_u	C C C S	v $M \perp$	$\omega_{5,6}$	γ_1 δ_1 ν_1		
	σ_x σ_y σ_z	Cyclobutan 1,3 dion, D_{2h}				
A_{1g}	S S S	p $1a$	ω_2 ω_3 ω_9	δ_1 ν_1		
A_{1u}	aa aa aa	v $1a$		γ_3		
B_{1g}	aa aa S	dp $1a$	ω_1 ω_8	γ_1		
B_{1u}	S S aa	v M_z	ω_1 ω_{10}	δ_2 ν_2		
B_{2g}	aa S aa	dp $1a$		δ_2 ν_2		
B_{2u}	S aa S	v M_y	ω_3 ω_{12}	γ_1		
B_{3g}	S aa aa	dp $1a$	ω_7	γ_2		
B_{3u}	aa S S	v M_x	ω_6 ω_{11}	δ_1 ν_1		
	σ_x σ_z	Cyclobutanon, C_{2v}				
A_1	S S	p M_y	ω_2 ω_3 ω_5 ω_6	γ_1 δ_1 ν_1 δ_1 ν_1		
A_2	aa aa	dp $1a$		γ_2 δ_2 ν γ_2		
B_1	aa S	dp M_x	ω_4 ω_8 ω_9	γ_1 δ_1 ν_1 γ_1		
B_2	S aa	dp M_z	ω_1 ω_7	γ_2 δ_2 ν_2 δ_2 ν_2		
Typus	Symmetrie	Auswahl	Kette	CH		

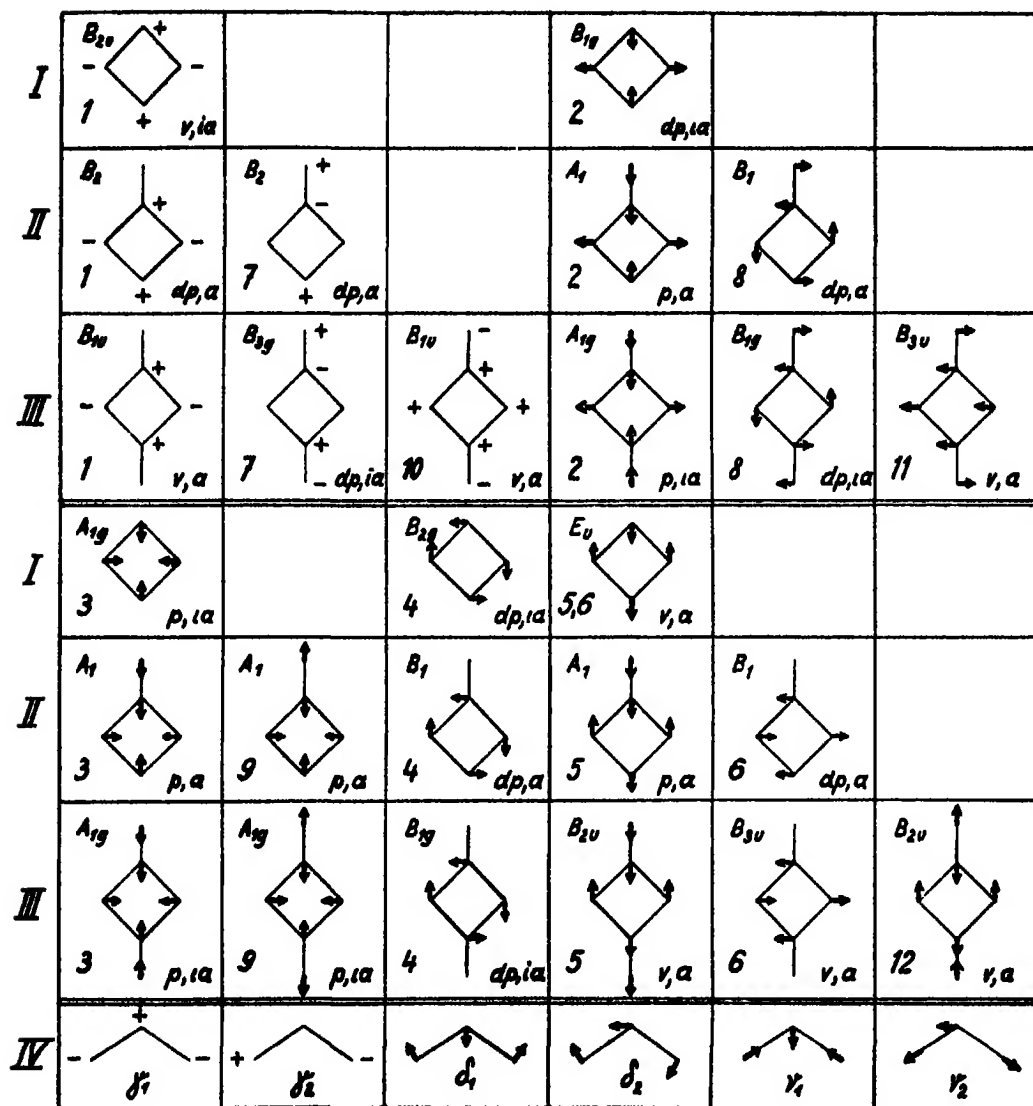


FIG 1

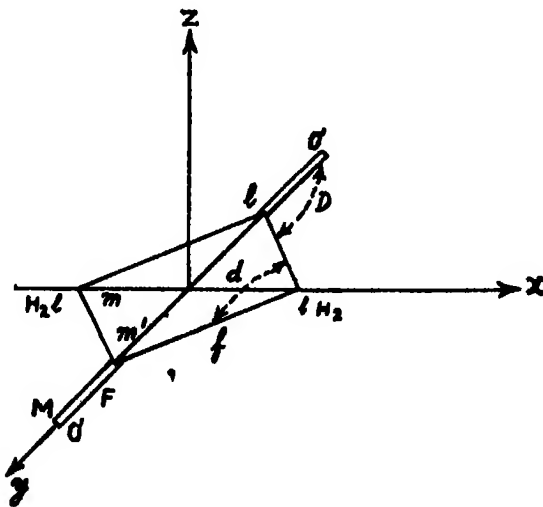
I, II, III schematisierte Formen der Kettenschwingungen von Cyclobutan, Cyclobutanon, Cyclobutan-1, 3-dion IV. Schwingungsformen der einzelnen Methylen-Gruppen, durch Zusammensetzung gleichphasiger Formen mit verschiedenen Phasen entstehen die "CH-Schwingungen" des Moleküls.

Beim Uebergang von Cyclobutan zum 1,3-Dion verschwindet erstens die C_4^s -Achse, die senkrecht zur Molekülebene σ_x zu denken ist, zweitens treten in der σ_x -Ebene an die Stelle zweier Methylen-Gruppen die beiden

C O-Bindungen Das hat zur Folge Erstens, dass einerseits alle in D_{4h} nur in Bezug auf C_4 verschiedenen Schwingungs-typen (d. h. A_{1g} und B_{1g} , A_{2g} und B_{2g} , A_{1u} und B_{1u} , A_{2u} und B_{2u}) ununterschiedbar werden und andererseits die entarteten Formen E_g bzw. E_u aufspalten in B_{2g} und B_{3g} bzw. B_{2u} und B_{3u} . Zweitens, daß je 4 $\gamma(CH)$, $\delta(CH)$, $\nu(CH)$ Frequenzen zu Gunsten der neu auftretenden Ketten-Schwingungen ω_4 bis ω_{12} verschwinden.

Beim Uebergang von 1,3-Dion zum Cyclobutanon verschwindet die σ_y -Ebene und damit alle auf ihrem Vorhandensein beruhenden Unterscheidungs-Merkmale, so dass die Schwingungs-Typen A_{1g} und B_{2u} zu A_1 , B_{1g} und B_{3u} zu B_1 , A_{1u} und B_{3g} zu A_2 , B_{1u} und B_{3g} zu B_2 verschmelzen. Je zwei $\gamma(CH)$, $\delta(CH)$, $\nu(CH)$ (in Tab 3 rechts aussen dazugeschrieben) treten neu hinzu, dafür verschwinden mit der einen C O-Gruppe die Kettenschwingungen ω_{10} , ω_{11} , ω_{12} .

(b) *Der zu erwartende Spektral-Typus* Um einen ungefähren Ueberblick zu erhalten, wie sich der spektrale Typus beim Uebergang Cyclobutan \rightarrow Cyclobutanon-Cyclobutan-1,3-Dion ändert, wurden die einschlägigen Formeln



des Valenz-Kraft-Systems (vergl die vorangehende Mitteilung von F Trenkler) mit folgenden Modell-Konstanten ausgewertet $F = 11,9$, $f = 4,67$, $D = 1,19$, $d = 0,467 \cdot 10^6$ Dyn/cm, $M = 16$, $m' = 12$, $m = 14$. Dabei wurden die Wurzeln der bei Cyclobutanon auftretenden Gleichung 4 ten Grades $g(x) = x^4 - a_1 x^3 + a_2 x^2 - a_3 x + a_4 = 0$ mit $x = n^2 \cdot 10^{-6}$ nach den Graefé'schen Näherungs-Verfahren in folgender Art bestimmt. Aus $g(x)$ wird durch Multiplikation mit $(-1)^4 \cdot g(-x)$ eine Gleichung 8 ten Grades $x^8 + b_1 x^6 + b_2 x^4 + b_3 x^2 + b_4 = 0$ mit $b_1 = 2 a_2 - a_1^2$, $b_2 = 2 a_4 + a_2^2 - 2 a_1 a_3$

$b_3 = 2 a_2 a_4 - a_3^2$, $b_4 = a_4^2$ gebildet. Aus dieser durch gleiche Behandlung eine Gleichung 16 ten Grades u so f, bis die Koeffizienten $2 a_2$, $2 a_4 - 2 a_1 a_3$, $2 a_2 a_4$ klein gegen a_1^2 , a_3^2 , a_4^2 werden derart, dass die Koeffizienten einer folgenden Gleichung gleich den Quadraten der Koeffizienten der vorangehenden Gleichung sind. Dann sind die Wurzeln der Gleichung soweit auseinander gezogen, dass bis auf kleine Fehler gilt $x_1 = -k_1/k_0$, $x_2 = -k_2/k_1$, $x_3 = -k_3/k_2$, $x_4 = -k_4/k_3$, mit $k_0 = 1$. Ergebnis der Rechnung in Tab IV

TABELLE IV

Berechnete Ketten Frequenzen der Valenzkraft-Modelle von I Cyclobutan, II Cyclobutanon, III Cyclobutan 1,3-Dion

	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_{11}	ω_{12}
I	674	1066	1066	1169				
II	666	918	1241	1155	1307	676	1933	
III	598	974	1365	985	1623	884	1922	1945

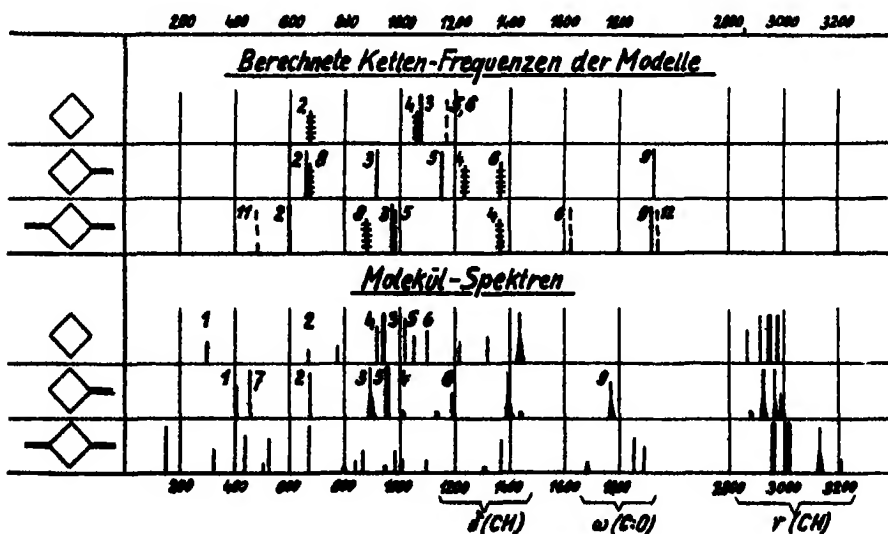


FIG. 2.

Oberes Feld: Berechnete Ketten-Spektren (ebene Schwingungen) der Modelle von Cyclobutan, Cyclobutanon, Cyclobutan-1, 3-Dion. Quergestrichelte Linien werden depolarisiert erwartet, längsgestrichelte sollen im Raman-Spektrum nicht auftreten. Die beigeetzten Ziffern entsprechen der in Figur 1 für die Schwingungs-Formen gewählten Bezifferung.

Unteres Feld: Die entsprechenden Molekül-Spektren, die durch die beigeetzten Ziffern getroffene Zuordnung ist nur als versuchsweise zu werten. Das Spektrum des Cyclobutans selbst wurde nicht direkt beobachtet sondern als Radicalspektrum aus den Spektren verschiedener Derivate abgeleitet.

(c) *Vergleich von Erwartung und Beobachtung* Misslich für den durchzuführenden Vergleich ist es, dass für die drei Moleküle weder Ultrarotspektren noch Polarisations-Messungen in Raman-Spektrum vorliegen und dass das aus den Spektren von Cyclobutanderivaten abgeleitete²-Cyclobutan-Spektrum nicht zu C_4H_8 sondern zu dem in der Symmetrie gestörten Radical C_4H_7 gehört. Es fehlen also massgebliche Kriterien und man kann nur aus der Zahl der Ramanlinien und aus ihrer Frequenz- und Intensitäts-Verteilung Rückschlüsse ziehen. Danach beurteilt kommt man zu dem Schluss, dass sich zwar das Spektrum des Cyclobutan's und Cyclobutanons mit der Erwartung vereinbaren lässt (vergl. die versuchsweise Zuordnung in Fig. 2), nicht aber das des Cyclobutan-1,3-Dions.

Hatte letzteres die Struktur eines 1,3-Dions, dann waren nach Tab. III von den 24 möglichen Schwingungs-Formen (12 zur Kette, 12 zu CH gehorig) nur 12 Raman-aktiv, nämlich die Kettenschwingungen $\omega_2, \omega_3, \omega_6$ (pol) und $\omega_4, \omega_7, \omega_8$ (depol) sowie je zwei $\gamma(CH), \delta(CH), \nu(CH)$ -Schwingungen. Beobachtet wurden jedoch 22 Linien, darunter 4 $\nu(CH)$ -Frequenzen statt der erwarteten zwei und 2 bis 3 C—O-Frequenzen statt nur einer.

Daraus folgt, Entweder liegt nur eine einzige Molekülform vor, dann muss sie so nieder-symmetrisch sein, dass alle Schwingungs-Formen Raman-aktiv sind. Oder es existieren zwei oder mehr Molekülformen in messbaren Mengen nebeneinander.

Im ersteren Fall würde in der Tat die Keto-Enol-Form eine hinreichend niedere Symmetrie besitzen. Wurde sie aber, so wie es A. L. F. F. W. aus den Dipolmoment-Messungen folgern, die dem Prozentsatz nach dominierende Form sein, dann waren zwar 24 Linien zu erwarten, doch konnte man weder das Auftreten von zwei CO-Frequenzen 1856 und 1891, noch das Auftreten von zwei erhöhten CH-Frequenzen 3131 und 3213 erklären, ußerdem würde das für die konjugierte Gruppe C—CH—C—O so uberaus charakteristische Merkmal der abnorm starken Intensitäts-Erhöhung der beiden Doppelbindungs-Linien fehlen. Wir halten diese nicht zutreffenden Kriterien für vollkommen ausreichend, um den von den englischen Autoren gezogenen Schluss, das Molekül läge vorwiegend in der Mono-Enol-Form vor, als mit seinem Raman-Spektrum unverträglich, abzulehnen.

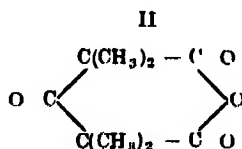
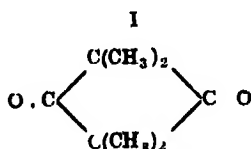
Aus dem Umstande, dass beim Uebergang Cyclobutanon \rightarrow Cyclobutan-dion die Linienzahl im Spektrum sich vermehrt statt vermindert, dass ferner 4 stark verschiedene CH-Valenz-Frequenzen und mindestens 3 Doppelbindungs-Frequenzen beobachtet werden, wird man vielmehr wohl schliessen

² K. W. F. Kohlrausch, R. Skrabal, *Mh. Chem.*, 1937, 70, 44.

müssen, dass zwei oder mehr Formen nebeneinander existieren. Darunter kann natürlich auch die Mono-Enol-Form sein, sie sollte eine wegen Ringspannung^{4, 5} sowohl, als wegen OH-Substitution⁶ stark erniedrigte C—C-Frequenz (also eher 1373 als 1686 l) und eine einerseits wegen Konjugation erniedrigte, andererseits wegen Ringspannung erhöhte⁷ C—O-Frequenz aufweisen. Aber mit Rücksicht auf deren infolge Konjugation zu erwartende hohe Intensität müssen wir nochmals betonen. Die Intensität der hierfür in Frage kommenden Linien gestattet es nicht, einen auch nur annähernd so hohen Prozentsatz Mono-Enol-Form anzunehmen, dass mit ihm die Höhe des beobachteten Dipolmoments zu erklären wäre.

In dieser Hinsicht besteht derzeit ein Widerspruch zwischen den Aussagen der physikalischen Methoden, solange man sich darauf beschränkt, nur die eingangs erwähnten Formen A, B, C in Betracht zu ziehen. Wir begnügen uns mit dieser Feststellung, da es uns nicht gelungen ist ein für die Notwendigkeit der Diskussion auch anderer Molekülformen wichtiges Beweis-Stück beizubringen, nämlich das Spektrum des *tetramethylierten* und damit fixierten und nicht zur Tautomerie fähigen Cyclobutan-1,3-dions.

IV Die Versuche zur Darstellung des 1,1-3,3-Tetramethyl-Cyclobutan-2,4-dion mussten wir vorzeitig abbrechen, da der eine von uns (R. Skr.) seine Arbeitsstätte veränderte. Wir folgten den Angaben von H. Staudinger,⁸ der vom Dimethyl-malonsäure-anhydrid ausgeht. Beim Erhitzen desselben in der Bombe erhielt er nahezu quantitativ das Cyclobutan-derivat, I, während beim Zusatz von Trimethyl-amin als Katalysator ein Produkt entsteht, das um ein CO₂ mehr enthält und als Tetramethyl-aceton-dicarbon-säure-anhydrid II aufgefasst wird.



Trotz Variation der Versuchsbedingungen (verschiedene Glassorte des Bombenrohres, verschieden lange Trocknung des Dimethyl-malonsäure-anhydrides, Zusatz von NH₄Cl als Katalysator) erhielten wir jedoch stets

⁴ K. W. F. Kohlrausch, R. Sika, *Ber. Dtsch. chem. Ges.*, 1936, **69**, 729, I. V.

⁵ L. Kahovec, K. W. F. Kohlrausch, *Zschr. Elektrochem.*, 1937, **43**, 285.

⁶ K. W. F. Kohlrausch, A. Pongratz, *Ber. Dtsch. chem. Ges.*, 1934, **67**, 1465.

⁷ K. W. F. Kohlrausch, R. Skrabal, *Zschr. Elektrochem.*, 1937, **43**, 282.

⁸ H. Staudinger, *Helv. chim. Acta*, 1925, **8**, 306.

fast ausschließlich die Substanz II neben wechselnden nur gerigen Mengen der Substanz I. Substanz II sollte ein sehr instabiler Körper sein, der beim Erhitzen unter Druck oder beim Kochen mit alkoholischem HCl leicht unter CO-Abspaltung in I übergeht. Wir haben grössere Mengen des Anhydrides II mehrmals im Vakuum destilliert, 6 Stunden in der Bombe auf 180° erhitzt, 14 Stunden im geschmolzenen Zustand in der Raman-Apparatur belichtet, ohne eine Zersetzung beobachten zu können, beim kochen mit alkoholischem HCl erhielten wir kein krystallisierendes Produkt, sondern ein Gemisch von Estern.

Die schmerzlichste Enttäuschung war aber, daß die Spektren der geringen erhaltenen Mengen der Substanz I (Fp 114° , Lit 116°) und die der Substanz II (Fp $78-79^{\circ}$), die beide am geschmolzenen Zustand gewonnen wurden (I Pl 2185 mF, 2187 mF, 2188 oF, 2189 oF., $t = 14$ bis 9 , $\vartheta = 120^{\circ}$, II Pl 2246, mF $t = 14$, $\vartheta = 85^{\circ}$), einander so ähnlich waren, daß wir an der Verwendbarkeit der Ergebnisse zweifeln und weitere Versuche abwarten müssen. Die gefundenen Ramanspektren waren

13

I	156 (6 b) ($\pm e$),	207 (1) (e),	241 (3) (e),	294 (3) (k, $\pm e$),	.	434 (0) (e),	480 (3) (k, e)
II	151 (2) ($\pm e$),	198 (1) ($\pm e$),	254 (1) ($\pm e$),	312 (3 b) ($\pm e$),	357 (3) (e)	428 (1) (e, e),	476 (1) (e, e)
I	510 (0) (e),	584 (6 b) (k, f $\pm e$),	630 (5) (k $\pm e$),		.	887 (1) (k, e),	
II	502 (00) (e),	590 (5 b) (f, $\pm e$, e),		687 (3) (e),	753 (1) (e, e),	858 (3) (f, e),	
I	928 (0) (k, e),	956 (1) (k, e),	1035 (3) (k, e),	1051 (1) (e),	1069 (1) (e),	1098 (2) (k, e),	
II	921 (2) (e),	976 (1) (e),			1060 (1) (e),	.	
I	1156 (1) (e),	1276 (1) (k, e),	1322 (3) (k),	1358 (1) (k),	1384 (1) (k, e),	1453 (4 b) (k, e),	
II	1175 (2) (e);				1379 (3) (e),	1451 (3 b) (e);	
I	1472 (2) (k, e),	1713 \pm 8 (5 b) (e),	1763 (0) (e),	1815 (3) (e),	2868 (2) (k, e),	2925 (6 b) (k, 1, e),	
II		1711 \pm 10 (5 b) (e),	1761 (1) (e),	1807 (3 b) (e),		2921 (2) (e),	
I	2973 (3) (k, e),	2986 (2) (k),					
II	2945 (0),	3001 (1) (e)					

14

STUDIEN ZUM RAMAN-EFFEKT.

Mitteilung XCIII · Cyclobutan-1,2-dicarbonsäuren und Abkommlinge

VON K W F KOHLRAUSCH

UND

R SABATHY

(180, Mitteilung aus dem physikalischen Institut der Technischen Hochschule Graz)

(Mit 1 Figur im Text)

DIE ersten Angaben über die Cyclobutan-1, 2-dicarbonsäuren (Formel-Bilder findet man im Anhang) stammen von W H Perkin jr¹, er erhielt bei der Decarboxylierung der Cyclobutan-1, 1-2, 2-tetracarbonsäure ein Gemenge von cis Cyclobutan-1, 2-dicarbonsäure und deren Anhydrid. Durch Behandlung mit Acetylchlorid wurde das Gemisch völlig in das Anhydrid (Fp² 77°) übergeführt und aus diesem die cis-Säure (Fp 137–138°) rein gewonnen, diese geht bei Erhitzen mit konzentrierter Salzsäure in die trans-Form (Fp 130°) über, deren Konfiguration später von Goldsworthy³ durch die Spaltung in die optischen Antipoden sicher gestellt wurde. In neuerer Zeit untersuchten Kuhn-Wassermann⁴ die Cyclobutan-1, 2-dicarbonsäuren, sie erhielten trotz genauer Befolgung der Perkin'schen Darstellungs-Vorschrift weder die durch Fp 137–138° charakterisierte Säure, noch das daraus herstellbare Anhydrid, sie fanden vielmehr eine Säure mit Fp 97–98°, die sie als cis-Säure ansprachen, während die beiden Perkin'schen Säuren als untereinander gleich und als trans-Form anzusehen seien. Diese Ansicht wurde gestützt durch den Vergleich verschiedener physikalisch-chemischer Daten mit denen anderer Polymethylen-1,2-dicarbonsäuren. In der Folgezeit gelang es Fuson⁵ und Mitarbeiter aus der Cyclobutan-1, 1, 2-tricarbonsäure durch Decarboxylierung ein Dicarbonsäure-Gemisch mit dem Fp 98–115° herzustellen, aus dem sie nach dem Perkin'schen Verfahren sowohl die cis-Säure (Fp 138–139°), als auch die trans-Säure (Fp 129–130°) gewannen. Weiters werden die Perkin'schen Angaben durch Bode⁶ bestätigt, der aus der Cyclobutan-tetracarbonsäure nach dem Vorgange Perkin's das Dicarbonsäureanhydrid (Fp 76–77°), die cis-Säure (Fp 138–139°) und die trans-Säure

¹ W H Perkin jr, *J Chem Soc*, London, 1894, 65, 572

² vergl Lennon u Perkin, *Zentralblatt*, 1928, 2, 647

³ L J Goldsworthy, *J Chem Soc*, London, 1924 125, 2013

⁴ R Kuhn und A Wassermann, *Helvetica chim. Acta*, 1928, 11, 600.

⁵ R C. Fuson, und Tai Yu Kao, *Amer chem Soc*, 1929, 55, 1536, R C. Fuson, und E Ellingboe, *Zentralblatt*, 1935, 1, 52

⁶ H. Bode, *Ber Deutsch chem. Ges.*, 1931, 67, 332

(Fp 130°) erhielt, die von Kuhn-Wassermann gefundene Saure mit Fp 98° konnte er nicht feststellen. Im "Richter-Anschütz" (1935) wird die ganze Angelegenheit etwas kurz abgetan mit der Bemerkung, daß die cis-Saure in zwei Formen mit Fp 91-98° und 139° existiere.

Obige kurze Darstellung der chemischen Geschichte der Cyclobutan-1, 2-dicarbonsäuren schien uns im Hinblick auf die Ergebnisse der hier durchgeführten spektroskopischen Untersuchung notwendig. Wir haben (vergleiche den Anhang) nach dem Perkin'schen Verfahren die cis- und trans-Säure, deren Methyl- und Äthylester, das cis-Anhydrid und das trans-Diamid hergestellt und die Ramanspektren dieser sechs Substanzen erstmalig aufgenommen. Die Fusions- und Siede-Punkte standen in hinreichender Übereinstimmung mit den ursprünglichen Perkin'schen Angaben, die diesbezüglichen Zahlenangaben, ferner jene für die Brechungsindizes der Ester und für die Ramanspektren sind im Anhang zusammengestellt. Einen graphischen Überblick über die Spektren gibt Fig. 1.

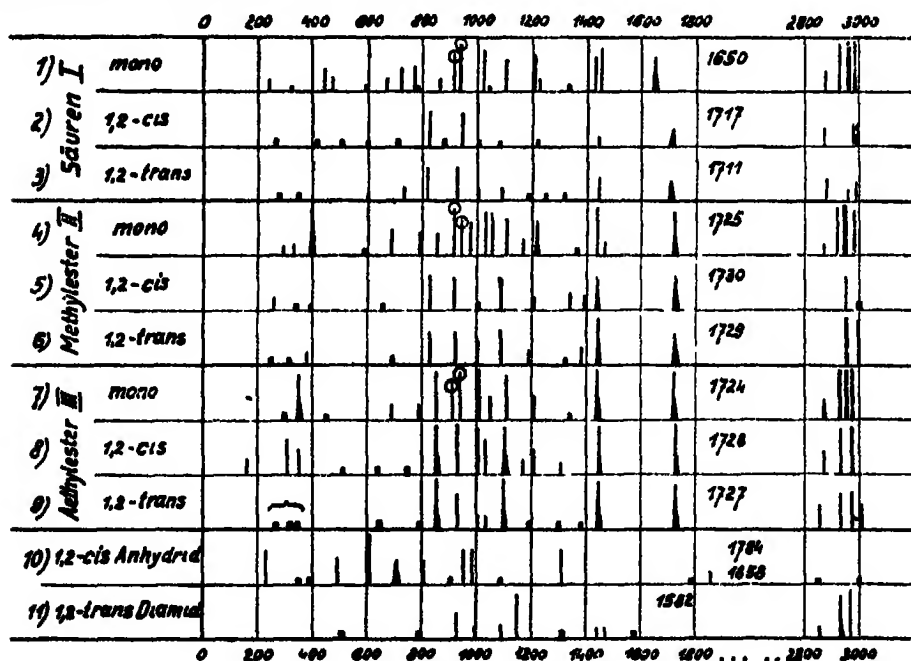


FIG. 1.

Die Ramanspektren von Cyclobutan-monocarbonsäure (1) und deren Methyl-(4) und Äthylester (7), cis-Cyclobutan-1, 2-dicarbonsäure (2) deren Dimethyl-(5), Diäthylester (8) und Anhydrid (10); trans-Cyclobutan-1, 2-dicarbonsäure (3), deren Dimethyl-(6), Diäthylester (9) und Diamid (11). Die Spektren von Nr. 1, 4, 5, 6, 7, 8, 9 wurden am homogenen flüssigen Zustand, die Spektren Nr. 2, 3 an wässriger Lösung, die Spektren Nr. 10, 11 am Kristallpulver gewonnen. Nicht eingezeichnet wurden in das Spektrum Nr. 11 die NH-Frequenzen $\Delta\nu = 3152$ (3 b), 3249 (0), 3330 (3b).

Aus den Spektren der Fig 1 lassen sich folgende Aussagen ablesen .

(1) Die Ähnlichkeit im Typus der Spektren im Feld I (Säuren), Feld II (Methylester), Feld III (Aethylester) lässt schliessen, daß es sich um Derivate desselben Stammkörpers, des Cyclobutans handelt, insbesondere weisen alle Spektren die für den Vierer-Ring charakteristischen⁷ Linien bei $\Delta \nu \sim 940$ (bei den Monoderivaten doppelt und durch Ringelung 0 gekennzeichnet, bei den Diderivaten nur einfach) sowie die gegenüber den Pentamethylen-Derivaten schwach erhöhten CH-Valenz-Frequenzen auf

(2) Unerwartet ist es, daß sich der Wert der CO-Frequenzen in der Estern der zweibasischen Säuren um (im Mittel) 4 cm^{-1} gegenüber dem der einbasischen Säure erhöht, die Säuren des Feldes I sind in dieser Hinsicht nicht vergleichbar, da Spektrum 1 zur homogenen, also meist assoziierten Substanz, Spektrum 2 und 3 jedoch zur Lösung gehört

(3) Unerwartet ist es ferner, daß zwischen den Spektren der cis- und trans-Form auch in den Einzelheiten fast kein Unterschied besteht, während bei der cis- und trans-Form der Hexamethylen-1, 2-dicarbonensäure (Hexahydrophthalsäure) deutliche Unterschiede feststellbar waren⁸

Diese im Punkt (3) hervorgehobene spektrale Ähnlichkeit zwischen Nr 2 u d 3, Nr 5 und 6, Nr 8 und 9 ist so groß, daß man versucht sein konnte mit Kuhn und Wassermann zu schliessen, es handle sich um eine und dieselbe Raumform des Moleküles und zwar um die trans-Form, da sonst der Spaltungs-Versuch von Goldsworthy nicht hätte gelingen können Dieser Schluss wird aber widerlegt durch die Tatsache, daß das Spektrum Nr 10 mit seinen zwei typischen^{9, 10} CO-Frequenzen bei 1784 und 1858 offenbar zu einem Anhydrid gehört, da aus diesem durch Eindampfen mit Wasser die durch Fp 136° charakterisierte Säure gewonnen wurde, wird man dieser wohl die cis-Form zubilligen müssen

Der eigentliche Zweck dieser Untersuchung und der noch geplanten Untersuchungen an den analogen Derivaten von Cyclopentan und Cyclopropan war es, den Unterschied in den Ramanspektren der cis- und trans-Formen kennen zu lernen Nach obigem gelangt man nun zu dem etwas unerwarteten Ergebnis, daß im Falle der Cyclobutan-1, 2-dicarbonensäure und ihrer Ester ein solcher Unterschied nicht merkbar ist

⁷ K W F. Kohlrausch und R. Skrabal, *Monatshefte f. Chemie*, 1937, 70, 41

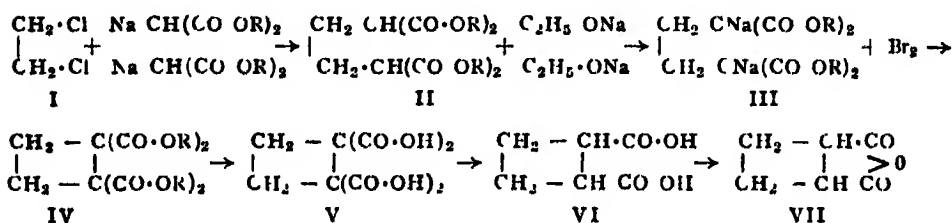
⁸ L. Kahovec und Mardaschew, *Ztschr. f. Elektrochemie*, 1937, 43, 288.

⁹ K W. F. Kohlrausch, A. Pongratz, und R. Seka, *Ber. Deutsch. chem. Ges.*, 1933, 66, 1.

¹⁰ L. Kahovec und K. W. F. Kohlrausch, *Ztschr f Elektrochemie*, 1937, 43, 285.

Anhang

Die Darstellung der Substanzen erfolgte nach *Perkin* (vergleiche die Einleitung), Aethylenchlorid I wurde durch Malonestersynthese in den 1, 1-4, 4-*n*-Butan-tetracarbonsäure-tetraethyl-ester II übergeführt, durch Einwirken von Brom auf dessen Dinatrium-Verbindung III wird der Ringschluss bewerkstelligt und der Cyclobutan-1, 1-2, 2-tetra-carbonsäure Ester IV erhalten. Dieser wurde durch Ba (OH)₂ verseift und aus dem Bariumsalz die Säure V in Freiheit gesetzt, nach mehrmaligem Umkristallisieren aus Wasser und Trocknung bei 100° wurde sie durch Erhitzen auf 180–190° decarboxyliert. Man erhält als Ausgangspunkt für das Weitere ein Gemisch von *cis*-Cyclobutan-1, 2-dicarbonsäure VI und deren Anhydrid VII.



(1) *Cis*-Cyclobutan-1, 2-dicarbonsäure-diäthylester C₄H₈ (CO OC₂H₅)₂ — Hergestellt aus der Säure VI durch eintägiges Stehenlassen mit absol. Alkohol + H₂SO₄ in der Kälte und nachträgliches kurzes Erhitzen auf dem Wasserbad. Dreimalige Destillation im Vakuum. K_p 114,5° (Lit. K_p+₃₀ 238–242°) n_D₂₀ = 1,4410. Aufnahme auf Pl. 2572, m F, t = 18, 2573, o F, t = 10, Ugd m bis st, Sp st, n = 50.

Δν = 164 (1) (e), 312 (3) (e), 355 (2) (k, e, c), 511 (0) (k, e, c), 643 (½) (k, e, c), 751 (½) (e, c), 856 (7 b) (k, f, e, c), 934 (5) (k, e), 1002 (4) (k, e), 1036 (3) (k, e), 1102 (5 b) (k, e), 1167 (1) (k, e), 1211 (2) (k, e), 1303 (1) (k, e), 1448 (8 b) (k, f, e), 1728 ± 7½ (5 b) (f, e), 2870 (2) (k, e), 2936 (4) (q, p, o, k, l, e), 2976 (12) (q, o, k, l, e).

(2) *Cis*-cyclobutan-1, 2-dicarbonsäure-dimethylester C₄H₈ (CO · OCH₃)₂. Darstellung analog wie beim Äthylester. Dreimalige Vakuumdestillation. K_p 101°, (Lit. K_p 225°), n_D₂₀ = 1,4442. Pl. 2574, und 2578, beide m F. Spalt 0,04, t = 32 und 18, Ugd st, Sp m, n = 15.

Δν = 258 (1) (e), 339 (½) (e), 392 (½) (e), 697 (½) (e), 828 (3) (e, c), 921 (3) (e), 1001 (½) (e), 1093 (3) (e), 1205 (1) (e), 1342 (1) (e), 1389 (1) (e), 1442 (3 b) (e), 1730 ± 8 (3) (e), 2957 (3) (e), 2998 (0) (e).

(3) *Cis*-cyclobutan-1, 2-dicarbonsäure-anhydrid (Formel VII) — Das Gemisch VI + VII wurde durch Acetylchlorid in das Anhydrid übergeführt. Zweimalige Vakuumdestillation, K_p 147–150° (Lit. K_p 270–273°), Fp 75°.

(Lit 77°) Hierauf noch zweimalige Destillation im Hochvakuum und Einschmelzen in H_2 -Atmosphäre in das Ramanrohr Pl 2587, m F, Spalt 0,06, $t = 14$, $\vartheta = 86^\circ$, Pl 2588, m F, Sp 0,04, $t = 32$, $\vartheta = 96^\circ$, Leichte Verfärbung nach rot Ugd st, Sp m, $n = 17$

$\Delta \nu = 233$ (3) (e), 349 (0) (e), 392 ($\frac{1}{2}$) (e), 494 (2) (\pm e), 614 (5) (\pm e), 712 (2 b) (\pm e), 804 (2) (e), 902 ($\frac{1}{2}$) (e), 949 (3) (e), 985 (3) (e), 1084 ($\frac{1}{2}$) (e), 1313 (3) (e), 1784 ($\frac{1}{2}$) (e), 1858 (1) (e), 2850 ($\frac{1}{2}$) (e), 2997 ($\frac{1}{2}$) (e)

(4) *Cis-cyclobutan-1, 2-dicarbonsäure* (Formel VI) Das Anhydrid Nr 3 wurde mit Wasser eingedampft, die Säure viermal aus H_2O umkristallisiert Fp 136° (Lit 137–138°) 2,55 g Säure wurden in 4,1 cm³ Wasser gelöst, mit Tierkohle auf 70° erhitzt und durch Blaubandfilter filtriert Pl 2662, m F, $t = 33$, Pl 2663, o F, $t = 24$, Ugd im zweiten Fall sehr st, Sp s, $n = 24$ Ergebnis unbefriedigend

$\Delta \nu = 263$ (00 ?) (e), 412 (0) (e), 502 ($\frac{1}{2}$) (e, c), 604 (00 ?) (e), 713 ($\frac{1}{2}$) (e), 824 (3) (c, c), 880 (0) (k, e), 944 (3) (k, e), 1003 (00) (k, e), 1079 (00) (e), 1220 (00) (e), 1443 (1) (e), 1717 ± 17 (1 b) (e), 2872 (2) (k, e), 2970 (2) (e), 2992 (2) (k, e)

(5) *Trans-cyclobutan-1, 2-dicarbonsäure* $C_4H_6 \cdot (CO OH)_2$ Die cis-Säure wurde durch Erhitzen (auf 190°) mit Salzsäure im Bombenrohr in die trans-Form umgelagert und mit Tierkohle aus Wasser umkristallisiert Fp 128° (Lit 130°) 2 g Säure wurden in 2 cm³ Leitfähigkeitswasser gelöst, mit Tierkohle auf 70° erwärmt, zweimal durch Blaubandfilter filtriert Pl Nr 2659, m F, Sp 0,06, $t = 24$, Pl 2660, o F, Sp 0,04, $t = 14$, letzteres wenig brauchbar, Ugd m, Sp s, $n = 23$

$\Delta \nu = 274$ (0) (e), 345 (0) (e), 604 (00) (e), 737 (1) (e), 816 (3) (k, e), 926 (3) (k, e), 1002 (1) (k, e), 1089 (1) (k, e), 1192 ($\frac{1}{2}$) (k, e), 1249 ($\frac{1}{2}$) (k, e), 1323 (00) (e), 1446 (2) (e), $1711 + 17\frac{1}{2}$ (2 b) (e), 2874 (2) (e), 2937 (1) (e), 2985 (1) (e)

(6) *Trans-cyclobutan-1, 2-dicarbonsäure-dimethylester* $C_4H_6 (CO OCH_3)_2$ Die trans-Säure Nr 5 wurde mit überschüssigem absol Methylalkohol versetzt und durch Einleiten von HCl bis zur Sättigung verestert, das Reaktionsprodukt in H_2O gegossen, 2 mal ausgeathert, die ätherische Lösung mit Wasser und Bicarbonat gewaschen, mit $CaCl_2$ getrocknet, Äetherrückstand zweimal im Vak destilliert Kp₁₃ 107° (Lit Kp ?), $n_{D_{18}^\circ} = 1,4451$ Pl 2628, m F, $t = 18$, Pl 2629, o F, $t = 12$, Ugd m bis st, Sp m, $n = 27$

$\Delta \nu = 253$ ($\frac{1}{2}$) (e), 317 ($\frac{1}{2}$) (e), 383 (1) (e), 699 ($\frac{1}{2}$) (e), 830 (3) (k, e, c), 922 (3) (k, e), 1001 (2) (e), 1098 (3) (k, e), 1193 (1) (e), 1327 ($\frac{1}{2}$) (k, e), 1382 (1) (e), 1445 (4 b) (k, e), 1729 ± 8 (3 b) (e), 2955 (8) (q, k, i, e), 2998 (4) (q, k, i, e)

(7) *Trans-cyclobutan-1, 2-dicarbonsäure-diäthylester* $C_4H_8 (CO \cdot OC_2H_5)_2$, Veresterung der trans-Säure analog wie bei Nr 6 Dreimalige Destillation im Vak Kp_{10} 118° , $n_{D17} = 1,4400$ Pl 2635, m F, $t = 18$, Pl 2636, o F, $t = 13$, letztere Aufnahme wenig brauchbar, Ugd m bis st, Sp m, $n = 29$

$\Delta \nu = [270 (00) (e), 319 (00) (e), 344 (00) (e)]$ (breite verwaschene Bande), 645 ($\frac{1}{2}$) (e), 798 (0) (k, e), 857 (5 b) (k, 1, e), 928 (3) (k, e), 1002 (1) (e), 1033 (1) (e), 1101 (5 b) (k, e), 1191 (00 ?) (e), 1295 (00 ?) (e), 1383 (0) (e), 1450 (5 b) (k, e), 1727 ± 14 (4 b) (e), 2858 (2) (e), 2938 (3) (q, k, e), 2976 (3) (q, k, e), 3017 (2) (e)

(8) *Trans-cyclobutan-1, 2-dicarbonsäure-diamid* $C_4H_8 (CO NH_2)_2$ — Die Ester der trans-Säure wurden mit überschüssigem konz wässrigem Ammoniak 3 Wochen stehen gelassen Das ausgeschiedene Diamid wurde aus Wasser umkristallisiert und getrocknet Fp $228-230^\circ$ (Lit 228°) Aufnahme in der Festkörperapparatur mit komplementären Filtern, Hgk-Erregung Pl F 83, $t = 24$, Pl F 84 $t = 48$ Schwaches Streuspektrum, $n = 17$

$\Delta \nu = 503 (\frac{1}{2})$, 790 (0), 925 (2), 1000 (1), 1091 (1), 1152 (4), 1314 ($\frac{1}{2}$), 1441 (1), 1471 (1), 1582 ($\frac{1}{2}$ b), 2857 (1), 2935 (4 b), 2973 (5), 3070 (0 ?), 3152 (3b), 3249 (0), 3330 (3 b)

THE ANOMALOUS DEPOLARISATION OF LIGHT-SCATTERING IN OPTICAL GLASSES.

BY R S KRISHNAN

(1851 Exhibition Scholar, Trinity College, Cambridge, England)

1. Introduction

It is now well known that optical glasses exhibit a characteristic scattering of light, comparable in intensity with that exhibited by an ordinary dust-free liquid, in many cases, the Tyndall cone is of a beautiful sky blue colour and nearly, but not quite completely polarised when viewed in a transverse direction. Lord Rayleigh (1919) who remarked on the phenomenon, was inclined to attribute it to spherical inclusions in the glass of diameter not small, compared with the wave-length of light and explained the finite depolarisation as due to the appreciable size of these inclusions. In his investigations on the scattering of light in solid and fluid media, Prof Raman (1922) took a different view, namely that the scattering in optical glasses arises fundamentally from the nature of the amorphous state of matter. He pointed out that we should expect two distinct types of scattering in amorphous solids, their relative importance depending on the particular circumstances of the case. The first type of scattering would result from the local (quasipermanent) fluctuations of optical density due to the non-uniform structure of the vitreous solid which differentiate it from the crystal; this type of scattering would, in respect of its intensity, be of the same order of magnitude as that arising from the (dynamic) fluctuations of optical density in the liquid at the temperature of fusion of the material. The second type of scattering would be due to the thermal agitation in the amorphous solid at the temperature of observation, and its intensity would be of the same order of magnitude as the light scattered in a crystal. In a later paper (Raman, 1927), he reported measurements of intensity and depolarisation of the light scattered transversely by a series of optical glasses, from which it appeared that low intensities and large depolarisations usually go hand in hand with low refractive indices, while glasses of high refractive indices generally give greater intensities and lower depolarisation. These results supported the view that the scattering is an intrinsic property of the glass. Very recently the author (Krishnan, 1936) made a comparative study of the light transversely scattered by seventeen different glasses of optical quality with the incident light in different states of polarisation, namely

unpolarised, vertically polarised and horizontally polarised. In all the cases studied, it is found that the values of the depolarisation factors ρ_u and ρ_v , corresponding to incident unpolarised light and light polarised with vibrations vertical respectively, are of the same order of magnitude as is usually observed in ordinary gases. On the other hand, when the incident light is polarised with vibrations horizontal, the horizontal component of the light scattered by the glass in the transverse horizontal direction, instead of being equal to the vertical component as in an ordinary gas or liquid, is definitely brighter than the vertical component, i.e., the depolarisation factor ρ_h is less than unity as in the case of emulsions and colloids containing particles whose size is not small compared with the wave-length of light. This anomalous depolarisation* has been explained by the author as due to the existence of molecular aggregates in glasses, of size not small compared with the wave-length of the incident light. The composition of the glass is found to have a marked influence on the formation and the size of these molecular aggregates.

In a paper on the theory of the scattering of light, Hans Mueller (1938) has discussed the author's investigations on glasses in great detail. He has proposed a new theory of the scattering of light in glasses, based on the assumption that glasses contain a random distribution of frozen-in-strains. Slightly below the solidification temperature these strains are normal ones, but at lower temperatures shearing strains are created due to temperature contraction. It is remarkable to find that the magnitude of ρ_h as observed by the author follows very closely the order predicted by the theory. Mueller's paper serves to emphasise the fundamental character of the anomalous depolarisation (i.e., ρ_h is less than 1), in relation to the study of the structure of amorphous substances.

Anomalous depolarisation is easily to be noticed in ordinary colloids, but is rather difficult to observe in optical glasses since the value of ρ_h is not far different from unity. The observation is rendered the more difficult by the feeble intensity of the light scattered in the transverse horizontal direction when the incident light is polarised with vibrations horizontal, and also by the feeble fluorescence exhibited by the optical glasses. Consequently in the earlier investigations, no attempt was made by the author to demonstrate the existence of anomalous depolarisation in an objective manner.

* Any value of ρ_h less than unity is termed as the anomalous depolarisation. ρ_h is defined as the ratio of the intensity of the vertical to that of the horizontal component of the scattered light when the incident beam is polarised with vibrations horizontal.

as distinct from purely subjective (visual) measurements. But in view of the importance of the subject in relation to Mueller's theory of glass structure, it was thought desirable to have an objective demonstration of anomalous depolarisation in optical glasses.

2 Experimental Details and Results

Two methods both based on photographic photometry are available for detecting the existence of anomalous depolarisation in any scattering medium. In the first method the transversely scattered light is photographed with the aid of two double-image prisms, one in the path of the incident beam and the other in the path of the scattered light. Of the four tracks thus obtained on the negative, corresponding to the four components V_v , H_v , V_h and H_h ,† the two middle ones should always be equal. If the fourth component H_h which is the horizontal component of the scattered light arising from the horizontal component of the incident beam is found to be distinctly brighter than either of the two middle anisotropic components, ρ_h will be greater than unity, from which it can be inferred that the optical heterogeneity of the scattering medium cannot be identified as due to the individual molecules, but due to small groups of molecules or due to the "frozen-in-strains" as Mueller has suggested. This method is not suitable for the case of optical glasses for the following reasons. The first component V_v is many times more intense than the other components. In consequence, the first component becomes enormously overexposed before a measurable record of the remaining three is obtained. The photographic halation produced thereby affects the intensity of the neighbouring components in such a way as to upset the equality of the middle two components and to equalise the last two components, namely, V_h and H_h , i.e., to make ρ_h tend to unity. The detection of the small difference in the intensities of the two components V_h and H_h is thus rendered difficult.

The second method which is employed in the present investigation consists in photographing the scattered light through a double-image prism using incident polarised light. A narrow beam of light of square section was passed through the glass under investigation, the incident light being polarised by means of a square-ended nicol. The light scattered transversely in the horizontal direction was observed through a double-image prism which was kept suitably orientated so as to separate the vertical and the horizontal components of the scattered light in a vertical plane. Photographs of the

† These symbols have the same significance as those given in *Proc Ind Acad. Sci.*, (A), 1938, 1, 782

two tracks were taken on the same negative for five different orientations of the nicol about the mean horizontal position. The corresponding nicol readings in degrees were 208, 203, 201, 199 and 194, where the reading 201 corresponded to that position of the nicol for which the incident beam was polarised with vibrations horizontal. Each negative containing the five pairs of tracks was passed through a Moll microphotometer and the intensities of the two tracks in each pair were compared. Three glasses having melt numbers 23975, 23497 and 22608 and also a bulb containing dust-free ethyl ether were examined under identical conditions. The respective microphotometric records are reproduced in Figs 1 to 4.

For the glass 23975 when the nicol reading is 208 the vertical component of the scattered light is definitely brighter than the horizontal component (see Fig 1). As the nicol is rotated towards the horizontal position, the two components become equal in intensity and when the reading is 201, i.e., when the nicol is in the exact horizontal position, the horizontal component is definitely brighter than the vertical component thus giving rise to a value of ρ_h less than unity. When the nicol is rotated further in the same direction, the two components of the scattered light again become equal in intensity and for a further rotation of the nicol the vertical component becomes brighter than the horizontal component. The reversal of intensities of the two components is clearly seen in Figs 2 and 3. But it is not so very conspicuous as in Fig 1. This is what should be expected since the observed values of ρ_h for these two glasses are higher than that for glass 23975. The following table gives the comparative values of ρ_v , ρ_v and ρ_h for the three glasses and also for ether.

TABLE I

Scattering substance	ρ_v^*	ρ_v^*	ρ_h^*
Glass No 23975	0.012	0.0046	0.68
Glass No 23497	0.045	0.02	0.77
Glass No 22608	0.061	0.03	0.91
Ethyl ether	0.08	0.042	1.00

* These values are taken from *Proc Ind Acad Sci.* (A), 1936, 3, 216

The microphotometric record taken with ether does not exhibit any reversal in the relative brightness of the two components. For nicol readings

H ↑
V ↑

H ↑
V ↑

H ↑
V ↑

FIG. 1 — Glass No 23975

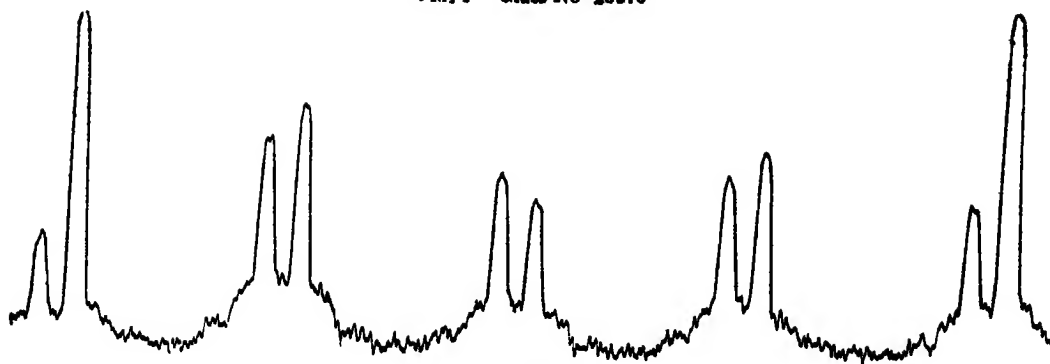


FIG. 2 — Glass No 23497



FIG. 3 — Glass No 22608

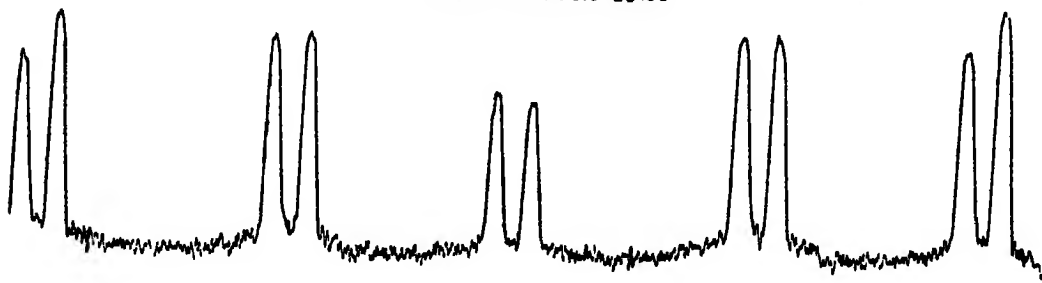
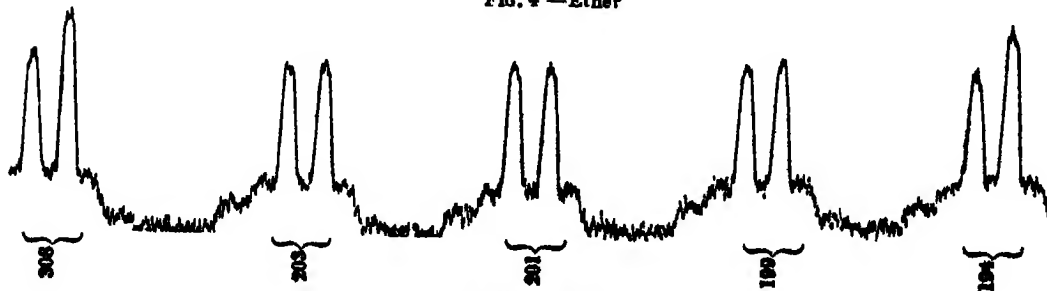


FIG. 4 — Ether



Nicol readings

194, 199, 203 and 208 the vertical component is definitely brighter than the horizontal component, whereas for nicol reading 201 the two are equal in intensity showing thereby that ρ_h has the limiting value of unity. This is in accordance with the theoretical considerations. From this it can be inferred that the anomalous depolarisation observed in the case of the three optical glasses investigated is a genuine effect and not due to any defect in the experimental technique. If suitable coloured filters are used to eliminate fluorescence, the reversal in the relative brightness of the two components can be seen more conspicuously.

In conclusion, the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman for his kind and helpful interest in the work.

3 Summary

An experimental method based on photographic photometry is described for demonstrating the existence of anomalous depolarisation, i.e., ρ_h less than unity, in optical glasses. Microphotometric records are reproduced which clearly show the existence of anomalous depolarisation in optical glasses. Three typical glasses are examined. The experiment was repeated with ether as the scattering substance and a negative result was obtained showing thereby that there was no defect in the experimental technique.

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LOW FREQUENCY RAMAN LINES IN ORGANIC CRYSTALS.

By C S VENKATESWARAN

IMMEDIATELY following the discovery of the Raman Effect by Prof Sir C V Raman in 1928, Krishnan in a Note to *Nature* (1928) reported six frequencies for crystalline quartz, out of which three namely, those at 127, 207 and 267 cm^{-1} , were attributed by him (1929) as characteristic of the crystal as a whole and distinct from the inner vibrations of the molecules in the crystal. He also observed (1929) similar low frequency Raman lines for calcite and gypsum. Later Krishnamurti (1930) showed that a sharp and intense line with frequency varying from 230 to 155 appears in the crystals of certain inorganic nitrates, but vanishes when they are examined in aqueous solutions. He has suggested therefrom that this frequency in the nitrates owes its origin to the mutual vibrations of the metal ions and the NO_3 ions in the crystal lattice and its magnitude depends upon the mass of the cation. The influence of increase of temperature on the position and character of the low frequency Raman lines studied by Brickwedde and Peters (1929) and Ornstein and Went (1935) also confirm the view that they are characteristic of the crystal lattice. In his investigations on the Raman spectra of calcite and aragonite Bhagavantam (1931) has further shown that the magnitude of these frequency shifts for the same chemical individual depends on its crystal structure.

Similar low frequency Raman lines in organic crystals with shifts ranging from 20 to 130 cm^{-1} were for the first time observed by Gross and Vuks (1935) in benzene, diphenyl ether, dibromobenzene and naphthalene. The fact that these lines in organic solids fall in the region where the 'wing' in the liquid appears, has led these authors (1936) to postulate that the latter is almost completely made up of these lattice Raman lines which become diffuse and merge with one another in the liquid state. These conclusions of Gross and Vuks regarding the origin of these lines in the crystals and their relation to the 'wing' in the corresponding liquids have been questioned by Sirkar. In a series of communications dealing with this subject, Sirkar and Gupta (1936-38) have put forward the suggestion that these low frequency lines owe their origin to intermolecular oscillations of polymerised groups of molecules in the solids, which are bound together by a weak electronic bond. The present investigation with organic crystals was

undertaken with a view to throw some light on the origin of these lines in crystals and their bearing on the 'wing' in liquids

Experimental

The substances examined were Kahlbaum's pure chemicals further purified by slow distillation in vacuum into the experimental tube. The molten liquid is cooled slowly till it sets into a translucent mass below the melting point. Though the solid thus obtained is polycrystalline, parasitic light is very much reduced in the scattered spectrum and reasonably good pictures are obtained with clear lines in the neighbourhood of the Rayleigh line. For an investigation of this character the choice of a proper spectrograph is of the utmost importance. Most of the spectrographs generally used for photographing Raman spectra possess a well-defined coma consisting of one or more broad bands on the Stokes side, round about 100 cm^{-1} from the Rayleigh line. This instrumental defect is shown markedly by several of even the high grade spectrographs installed in this laboratory. This coma is comparatively very feeble in the Hilger two-prism glass spectrograph and is noticeable only in very heavily exposed spectrum plates. The latter instrument was, therefore, used in the present investigation and care has been taken to eliminate errors arising from this defect. Though the dispersion of this spectrograph is only 22 \AA per mm in the 4046 \AA region, due to the large size of the prisms and lenses its resolving power is considerably greater than that of either the Fuess spectrograph having a dispersion of 18 \AA per mm used by Sirkar or the one employed by Gross and Vuks in their investigations. This has enabled the author to obtain correct estimates of the width of these lines at various temperatures. The temperature of the crystals is varied by means of an electric heater surrounding the whole of the experimental tube. The plates are measured with the aid of a Hilger cross-slide micrometer and the accuracy in the case of sharp lines is of the order of 1 cm^{-1} .

Results




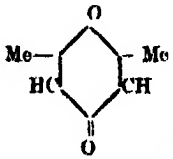
The results of the investigation are given in Table I* and some photographs of the spectra are reproduced in the accompanying plates. Table II gives the data on the low frequency Raman lines in organic crystals so far published by other authors.

The following observations may be made on the results obtained in the present investigation. All compounds containing the benzene nucleus yield in general four lines with frequency shifts ranging from 20 to 130 cm^{-1} .

* Note. The complete spectra of coumarin and dimethyl- γ pyrone as well as some of the other compounds will be reported in a separate communication.

TABLE I

Exciting Line $\lambda = 4046 \text{ \AA}$ For No 12 exciting line is 4358 \AA

No	Substance	Crystal and Molecular Structures	Temperature in °C	Raman Frequencies in cm^{-1}			
1	Phenol M P 41°C	Rhombic OH 	25°	38 (3)	72 (5 b)	93 (2 b)	116 (4 b)
			38°	One band with sharp edge ending at 110			
2	Benzoic acid M P 122°C	Monoclinic $\text{C}_6\text{H}_5\cdot\text{COOH}$	25°	38 (2)	62 (4)	101 (6)	126 (1 b)
3	Salicylic acid M P 154°C	Monoclinic OH $\text{C}_6\text{H}_4 \text{COOH}$	25°	43 (2)	64 (5)	95 (2)*	117 (1 b)*
4	Resorcinol M P 110°C	Rhombic OH 	25°		70 (5 a)	(Incomplete)	
5	Catechol M P 105°C	Monoclinic OH 	26°	36 (4)	56 (5)	78 (2)	110 (1)
			52°	36 (5)	55 (6)	77 (2)	108 (1)
			80°	35 (4)	55 (7)	77 (1)	108 (0)
6	<i>p</i> Dichloro benzene M P 53°C	Monoclinic $\text{C}_6\text{H}_4\text{Cl}_2$	25°		48 (0 b)		89 (6 b)
			45°		43 (6)	53 (5)	88 (5 b)
7	Phthalic acid M P 206°C	Rhombic $\text{C}_6\text{H}_4(\text{COOH})_2$	25°			81 (3)	
8	Dimethyl γ pyrone 		25°		48 (2 b)		101 (2 b)

* These two lines appear as a single broad band on the Stokes side

TABLE I (Contd.)

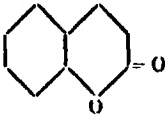


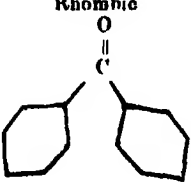
No	Substance	Crystal and Molecular Structures	Temperature in °C	Raman Frequencies			
9	Coumarin M P 71°	Rhombic 	25°	39 (5)	55 (6) 69 (2)	96 (5)	112 (5)
			60°	38 (5)	55 (6) 69 (1)	94 (4)	109 (4)
			68°	38 (5)	55 (6) 68 (1)	93 (4)	109 (4)
			70°	38 (5)	54 (6) 67 (1)	103 (2 b)	
10	Naphthalene M P 80°	Monoclinic 	25°	46 (5)	74 (10)	108 (4)	121 (2)
			65°	46 (4)	74 (10)	105 (4)	118 (2)
			75°	46 (3)	72 (10)	102 (3 b)	
11	Diphenyl M P 70° (C ₆ H ₅) ₂	Monoclinic 	25°	49 (3 b)	75 (2 b)		150 (1 b)
12	Benzophenone (C ₆ H ₅) ₂ C=O M P 48°	Rhombic 	25°		67 (3)		102 (3 s) 122 (1)
13	Salol M P 43°	Rhombic HO C ₆ H ₄ CO O C ₆ H ₅	25° -180° (glass)		71 (1 ?)	96 (5 s)	
				No lines and no wing			
14	Chloroacetic acid	Rhombic CH ₂ Cl COOH	25°		54 (2 s)		

TABLE II

No	Substance	Chemical Formulae	Temperature in °C	Raman Frequencies				Reference
1	Benzene	C_6H_6 (Rhombic prismatic)	— 0°		62 (4 b)		104 (2 b)	G and V *
	"	"	— 180°		81	98 (b)	125	S and G
2	Diphenyl ether	$(C_6H_5)_2O$ (Rhombic)		22 (8 s)	38 (2 s)	67 (8 b)	104 (10 b)	G and V * and S
3	Naphthalene	$C_{10}H_8$	0°	45 (4 s)	73 (8 b)	100 (3)	124 (2)	"
	"	"	— 180°		80	120	140	S
4	p Dibromo benzene	$C_6H_4 Br_2$ (Monoclinic)		20 (8)	38 (8)		93 (6 b)	G and V *
5	p Dichloro benzene	$C_6H_4 Cl_2$ (Monoclinic)	< 25°	27	46	54	93 (b)	V *
	"	"	> 33°		43	55	82 (b)	"
6	p Bromochloro benzene	$C_6H_4 Cl Br$ (Rhombic or monoclinic)		22	43		94 (b)	"
7	Chlorobenzene	C_6H_5Cl		49	67	80	105	S and G
8	Cyclohexane	C_6H_{12}			69		105	M
9	Dichloro ethylene	$CHCl CHCl$			53 (st)			S and G
10	Acetic acid	CH_3COOH			49 (v st)		119 (v w)	Sid
11	Chloroform	$CHCl_3$			75		94	S and G
12	Bromoform	$CHBr_3$ (Hexagonal)			32-55			Sid

G and V = Gross, E. and Vuks, M. V = Vuks, M, S = Sirkar, S C, S and G = Sirkar, S C, and Gupta, J, M = Mitra, S M; Sid = Sidoro'a, A I

* The numbers within brackets are estimates of relative intensities obtained from the published photographs.

provided the lines are fairly sharp and the spectrum is intense. There is a general similarity in their low frequency spectra and in most cases the fourth frequency which has a shift of more than 100 cm^{-1} is nearly double the second. The latter line which appears round about 60 cm^{-1} is one of the most intense lines of this group and in all cases it has greater intensity than the one preceding. Apart from these similarities, the magnitude of the frequencies varies from compound to compound.

As illustrated in the accompanying plates, the width of the lines also varies considerably with the nature of the substance. In coumarin, catechol, benzoic acid and salicylic acid all the lines except the outermost one are fairly sharp, in paradichlorobenzene and naphthalene they are broad and in diphenyl they are very broad. The great breadth of some of these lines may be due to their composite character. Sirkar has shown that at liquid air temperatures these lines sharpen just as other molecular vibrations themselves do. But on raising the temperature up to the melting point no appreciable effect is observed on the first two lines. The outermost frequency, however, shows a measurable diminution due to the expansion of the crystal and diffuses out slightly as illustrated in Figs 1 to 5. In passing over to the liquid state, there is a sudden transition, the lines being completely replaced by a wing whose intensity is great near the Rayleigh line. In phenol (Fig 2), four broad lines of almost equal intensity appear just resolved at the room temperature, but at 38°C , that is, just below the melting point, due to further broadening of the lines, the structure of the pattern is lost and instead, a band sharply ending at 110 cm^{-1} appears on the plate. The author is unable to confirm the change in the spectra of *p*-dichlorobenzene at less than 25°C and greater than 33°C reported by Vuks (1937) and attributed to change of crystal form, even though the substance was kept for well over a week at ice-cold temperature before the spectrum at 25°C was taken. The minor changes in the spectrum of this compound given in Table I are to be explained as caused by changes of temperature alone unaccompanied by change of crystal structure.

Liquid benzophenone in the supercooled state gives a well-defined band at 102 cm^{-1} corresponding to the sharp line in the solid in that position. The wing, however, is less prominent in the liquid. The persistence of this band in liquid benzophenone has also been previously observed by Gross and Vuks (1935). A similar observation has been made by the latter authors and by Sirkar (1936) for diphenyl ether. In diphenyl also, corresponding to the broad line at 150 in the solid, there is a band at 140 in the liquid (Mukerji, Aziz, 1938).

Distilled salol in vacuum remains in a transparent glassy state up to the liquid air temperatures. The glass softens to the liquid condition much below the melting point as the temperature is raised. The spectra of the light scattered by the glass at liquid air temperature and the liquid salol are given in Fig 7. In the glass a continuous spectrum is present which masks the Raman lines beyond 400 cm^{-1} to some extent. In spite of this fact, for the same intensity of the spectra of the glass and the liquid as judged from the intensity of the Raman lines of larger frequency shifts, the

glass shows neither a wing nor any line near the Rayleigh line, whereas the liquid gives a fairly intense wing characteristic of the liquid state. The crystals of salol prepared by the method described earlier form an opaque mass and yield Raman lines only on long exposures. Though under these conditions the region near 4046 \AA is affected by halation, one fairly intense and sharp line at 96 and one faint line at 70 could be identified on the plates

Discussion

Origin of low frequency Raman lines—The influence of temperature on these lines in the crystals and especially their total disappearance as discrete lines in liquids are characteristic features which suggest that they are not due to intramolecular vibrations but are intermolecular in origin. Gross and Vuks (1935) have attributed these lines to oscillations of the crystal lattice. Sirkar (1936) avers that the change in the polarisability involved in a lattice oscillation is too small to account for the great intensity of these lines as compared to the intense Raman lines of the molecule. He has also pointed out other considerations such as the persistence of these lines in some liquids and solutions, the differential changes in frequencies of various lines of one and the same crystal due to changes of temperature and the inadequacy of these lines to account for the heat content of these crystals by their Debye functions, as obstacles in the way of assigning them to crystal oscillations. Based mainly on his arguments against their lattice origin, he has suggested that they arise from intermolecular oscillations of polymerised groups in the solid.

The following considerations are, however, in favour of attributing these lines to lattice oscillations in the crystal. (1) The results given in Tables I and II show that in the case of benzene derivatives, though there are certain general similarities in the spectra, considerable variations occur in the magnitude, intensity and breadth of the respective lines due to changes both in the molecular structure and in crystal form. The change due to crystal structure alone is particularly noticeable in resorcinol and catechol having very similar chemical formulæ, the intense line at 70 cm^{-1} in the former appearing at 55 cm^{-1} in the latter. Benzoic acid and salicylic acid having similar crystal structures, on the other hand, show a small difference only in the intensities of the lines, which is due to the difference in their molecular formulæ. (2) In inorganic crystals of the ionic type the lattice Raman lines are known to fall in the region between 100 to 300 cm^{-1} . When the force between the oscillating mass points is valence as in diamond the frequency is very much higher. In the organic crystals belonging to the molecular type of lattices, the intermolecular forces are weaker than the electrostatic forces in ionic crystals and consequently the lattice frequencies

should be correspondingly lower. The experimentally observed Raman lines are of the expected magnitude. (3) It has been observed in a large number of organic crystals (Figs 1 to 5) that as the temperature is raised these lines retain almost the same breadth up to the melting point. In the case of ionic crystals, as far as it is known, these lines become more diffuse at higher temperatures. This is well illustrated by the beautiful photographs of the spectra of sodium nitrate taken at different temperatures by Nedungadi (1938). This difference in the behaviour of ionic and molecular crystals may be explained as follows. If A and B are two points connected together by a force f , the frequency of oscillation ν is given by $\nu = 2\pi \sqrt{f/m}$, where m is the reduced mass. In the case of ionic lattices the distance between the oscillating units is small and the force is great. During an oscillation, these two units, A and B approach and recede from each other and the force f varies between a maximum and a minimum. It is thus easy to see that ν will cease to be monochromatic and give rise to a broad Raman line. With the rise of temperature, this variation of force and consequently the breadth of the line will also increase. In the case of molecular lattices the distance between the mass points is generally larger and the force is less than for the ionic and the variation in the force during mutual oscillations of the units is relatively small, changes due to rise of temperature is negligible, provided the amplitude of the oscillations remains small, as is the case so long as the solid state is maintained. This accounts for the fact that no appreciable change is observed in the sharpness of the lattice lines in organic crystals in which only residual molecular forces are responsible for such oscillations. No proper explanation is possible for this difference in the behaviour of molecular and ionic crystals on the theory of polymerisations postulated by Sirkar. (4) It is significant to note that while salol crystals have yielded one sharp and fairly intense line at 96, no such line is observed in the glassy state. There is more likelihood of polymers existing in glasses than in crystals. The fact that the line is not recorded in the glass indicates that a crystalline lattice in which units are oscillating with definite phase relationship with each other is necessary to produce these low frequency lines.

Oscillations of molecules which constitute the mass-points of a crystal lattice can be produced by a displacement from an equilibrium position resulting from the intermolecular forces, either by a translation or by a rotation through small angles about the centre of gravity. The frequency of a translational oscillation is determined by the intermolecular forces and the masses of the oscillating units and that of a rotational oscillation depends on the moment of inertia of the molecule. As has been pointed out by Sirkar,

the mutual oscillations of either type of a single pair of molecules or groups of molecules may not produce sufficient change in polarisability to yield an intense Raman line in light scattering. But the crystal is an elastic continuum and the several units in the lattice oscillate with a definite phase relationship with each other. It may be assumed that at any instant during an oscillation when a molecule approaches the neighbouring molecule on one side, its opposite neighbour will be receding from it so as to maintain the centre of gravity. The cumulative effect of this is to render the change in polarisability in a finite volume sufficiently large to account for the appearance of intense Raman lines. The results of the present investigation indicate that the outermost lines at about 100 cm^{-1} are to some extent broad and diminish in frequency and diffuse out as temperature is increased up to the melting point. The lines nearer the Rayleigh, on the other hand, retain their sharpness and show proportionately small changes in frequency at these temperatures. The difference in the behaviour of these lines suggests that the outermost line is due to translational oscillations of the lattice and the intense lines of smaller frequencies are due to the flexural oscillations of the lattice involving 'hindered rotation' of molecules. The anomaly pointed out by Sirkar in the changes of these frequencies at different temperatures and in crystals of similar molecular structure is thus due to a difference in the nature of oscillations responsible for each of these lines. In a note to *Current Science*, the author (1937) pointed out that in the cubic crystals of CO_2 , the sharp line at 58 cm^{-1} agrees with the lattice frequency calculated from the Lindemann's formula and is of the same order of magnitude as the frequency of hindered rotation of the molecules calculated on the lines indicated by Pauling (1930) for linear molecules. This agreement has led to the suggestion that this line is due to a flexural oscillation of the lattice of the type indicated above. In a recent paper Sirkar and Gupta (1938) have criticised this view of the author on the basis that the heat content of solid CO_2 calculated from the Debye function of this frequency does not agree with the observed facts. Similar considerations have been advanced by them to rule out the lattice origin for the lines in sulphur and benzene. It may be pointed out that Debye functions are applicable only to *continuous* radiations having frequencies ranging from zero to a limiting value ν_m , the existence of which is demonstrated by the fine structure of the light scattered by solids (Raman and Venkateswaran, 1938). The lattice vibrations have a definite frequency and yield a *discrete* line just as the molecular vibrations do. Hence for the calculation of the specific heat of a solid, the Einstein functions of these frequencies are more appropriately applicable than the Debye functions. If calculations of specific heat are made on this basis, taking into account

the degeneracies involved in a particular oscillation, the discrepancy discovered by Sirkar and Gupta disappears

In relation to the wing in liquids—Gross and Vuks (1936) have postulated that the lattice Raman lines in solids broaden and give rise to the wing that is observed on either side of the Rayleigh line in liquids. The chief characteristics of this wing in liquids are its great intensity at or near the Rayleigh line and its rapid but continuous fall upto a limit which varies from liquid to liquid. It is prominent only in anisotropic molecules and is depolarised to an extent of $6/7$ throughout its entire region. Rao (1934) and Gross and Vuks (1935) have reported that there is no observable difference in the distribution of the intensity or its extension with the rise of temperature upto the boiling point, except in the region from 0 to 20 cm^{-1} where according to the latter authors there is an increase in intensity with rise of temperature for certain viscous liquids. Though on a rough estimate the wing in the liquids and the lines in the solids show some correspondence (Sidorova, 1937), careful examination of Figs 1, 2 and 3 will reveal important differences in the extent and distribution of intensity in either case. Thus in coumarin and naphthalene the lines exist up to 110 to 120 cm^{-1} whereas the wing, in equally exposed plates, extends only up to about 70 or 80 cm^{-1} . In phenol, the extension of the wing is greater than for the lines. Secondly, the line at about $50\text{--}60\text{ cm}^{-1}$ is the most intense in the lattice spectra, but the wing shows no maximum at this point. Thirdly, if the major portion of the wing in liquids is vibrational in origin, it has to be postulated that a quasi-crystalline structure exists in the liquids and remains the same upto the boiling point, in order to interpret the results obtained with the wing at higher temperatures satisfactorily. This is highly improbable. Fourthly, glass itself being a supercooled liquid, the discrete lines in the crystals should exhibit themselves either as a wing as in liquids or as broad bands. Author's results with salol, glass and liquid, conclusively show that this is contrary to facts (Fig 7). Fifthly, Gross and Vuks (1935) themselves have observed that these lattice Raman lines in solids show a depolarisation factor varying from $\rho = 0$ to $\rho = 1$, and this does not fit in with the observations of all investigators that the wing in liquids is depolarised to an extent of $6/7$ throughout its entire region. Sirkar and Gupta have also adduced other evidence to show that the wing and the low frequency Raman lines are not connected with each other. The obvious conclusion arising from these considerations is that the wing in liquids is an entirely independent manifestation of the properties of molecules in a state of rotation in a random fashion in the medium. The discrete lines arising from translational or flexural oscillations of the lattice cease to exist in the liquid, and the hundered

rotation of molecules involved in the flexural oscillations is replaced by complete rotation in the liquids, provided the viscosity is not very great. As suggested by Raman and Krishnan (1928), this molecular rotation gives rise to the wing in liquids, with a distribution of intensity similar to that observed by Bhagavantam and Rao (1934) and Weiler (1935) for gases above critical pressures.

There is one fact, however, which needs explanation. In liquids, benzophenone, diphenyl and diphenyl ether, a well-defined band appears in the place of the line above 100 cm^{-1} in the solids and is observed to persist even at high temperatures and in dilute solutions. These three compounds possess two benzene rings linked through a valence bond. According to the present author, this band arises from deformational oscillations of these two rings against each other and thus appears to be intramolecular in origin and have nothing to do with either the lattice oscillations as suggested by Gross and Vuks or with polymerisation as postulated by Sirkar. A similar oscillation which gives rise to a depolarised Raman band below 200 cm^{-1} has been observed by Saxena (1938) for bicyclic compounds.

In conclusion, the author desires to express his grateful thanks to Prof Sir C. V. Raman for his continued interest and valuable suggestions in the course of the work.

Summary

The Raman spectra of the low frequency region between 20 and 130 cm^{-1} have been recorded for fourteen organic solids and the influence of rise of temperature up to the melting point on these lines in a few cases has been investigated. These lines in the solids are interpreted as arising partly from translational and partly from rotational oscillations of the molecules with definite phase-relationship with each other in the lattice. Liquid salol exhibits a fairly intense wing near the Rayleigh line which does not appear in salol glass at liquid air temperature. This observation and other experimental facts such as extension of the wing, the distribution of intensity and the influence of temperature on it and the degree of depolarisation at different points in the wing and the corresponding lines in the solid do not support the hypothesis of Gross and Vuks that most of the wing in liquids arises from the lattice Raman lines and that the liquid state is quasi-crystalline in structure. A band observed in liquids, benzophenone, diphenyl ether and diphenyl in the place of a line above 100 cm^{-1} in the solids is attributed to a deformational oscillation in the molecule itself, which seems to be characteristic of bicyclic compounds.

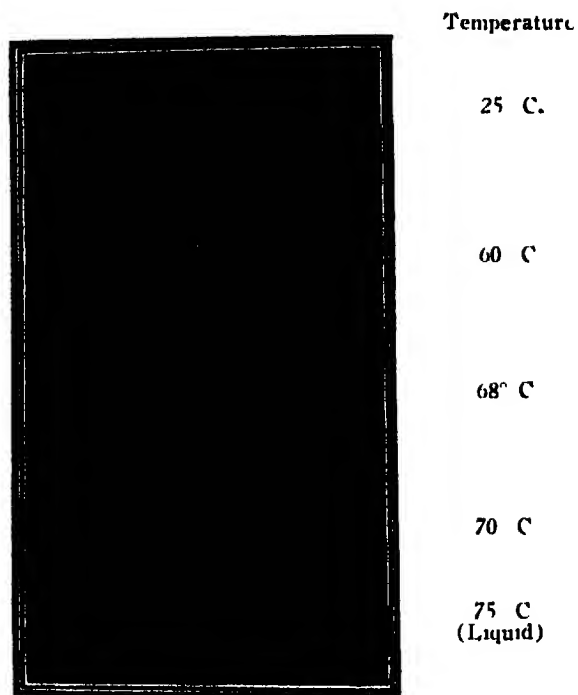


FIG 1. Coumarin

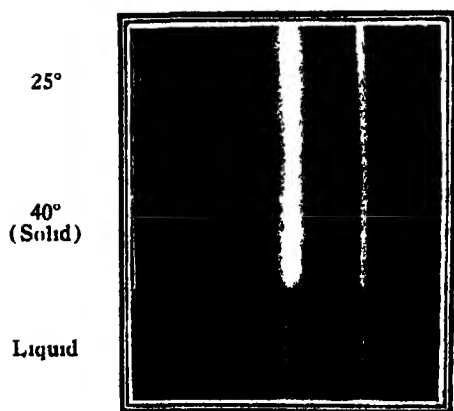


FIG 2. Phenol.

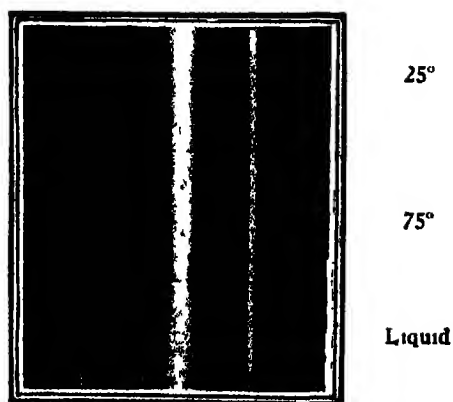


FIG 3. Naphthalene

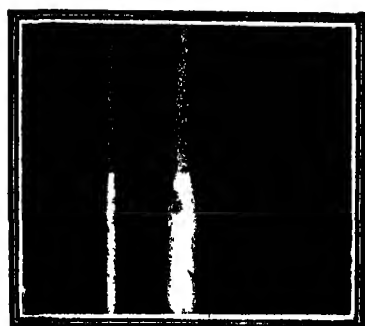


FIG 4 Catechol

25

90°



Benzoic
acid

Diphenyl

Do

FIG 6

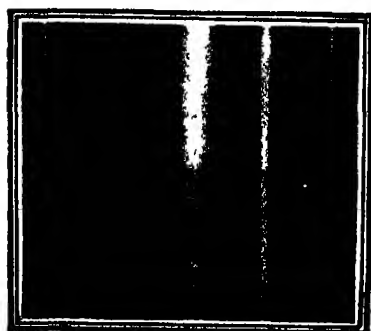
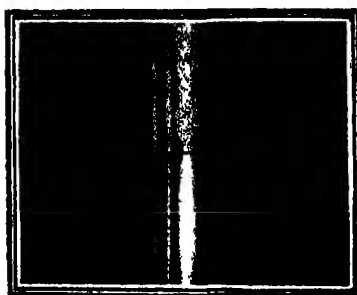


FIG 5 Dichlorobenzene

25

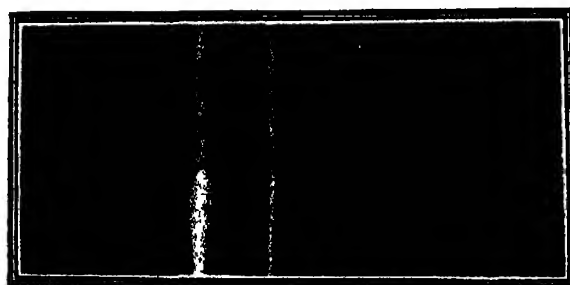
40°



Solid

Supercooled
Liquid

FIG 7 Benzophenone



Glass at 180° C

Liquid at 45° C

FIG 7 Salol

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DEPOLARISATION OF UNMODIFIED LIGHT-SCATTERING IN LIQUIDS.

BY BISHAMBHAR DAYAL SAXENA

1 Introduction

Experimental—One of the most easily observable facts concerning the diffusion of light in dust-free liquids is the partial polarisation of the transversely scattered light. This can be seen at once on viewing the path of a beam of light through a liquid with a double-image prism, and requires neither a monochromatic source nor a spectroscope. The defect of polarisation depends on the chemical nature of the liquid and on the temperature of observation, and quantitative measurements of it for a variety of substances are recorded in the earlier literature on light-scattering and especially in the careful and extensive investigations of K. S. Krishnan (1925). In the classical theory of light-scattering, the depolarisation is ascribed to the optical anisotropy of the molecules and their random orientation in the liquid. As the result of the discovery of the Raman effect in 1928, the subject has however assumed an entirely new complexion. When it is realised that the light scattered by a liquid includes a whole range of frequencies different from that of the incident light, it might seem at first sight that measurements of depolarisation made without a spectroscope have no significance. That this is not really the case and that the earlier measurements of depolarisation have an important bearing on the effects observed with the spectroscope was shown by Raman and Bhagavantam (1931) with the aid of a new technique devised by them, namely, the spectroscopic measurement of depolarisation with a slit of variable width. They showed that if the incident light is monochromatic and the polarisation of the transversely-scattered light is measured with the slit of the spectrograph *wide open*, the value of the depolarisation observed is sensibly the same as that obtained in the earlier (non-spectroscopic) observations. When, however, the slit is narrowed down, the depolarisation falls off, until finally with a very fine slit, it may reach a considerably lower value. This conclusion has been fully substantiated by the work of later observers, namely Venkateswaran (1932), Ranganadham (1932 and 1933) and Rousset (1935). The explanation of the results stated depends on a fact first noticed by Sir C. V. Raman (1928) namely that the spectrum of monochromatic light scattered by a liquid includes not only discrete lines, but in many cases also a continuous spectrum with a marked defect of polarisation. This continuous spectrum appears overlying the discrete lines in the spectrum and is especially

intense in their immediate neighbourhood. As the undisplaced lines are by far the strongest in the scattered light, the nebulosity which appears superposed on them is of correspondingly great intensity, and as it is depolarised to the maximum extent (6/7), its presence notably influences the defect of polarisation of the total scattered light. With the slit wide open, the image of an incident line as recorded on the photographic plate becomes broad enough to include within itself the whole region of sensible intensity in the continuous spectrum in its neighbourhood, and the observed depolarisation reaches a value practically the same as that obtained without the use of monochromatic light or a spectroscope. By reducing the slit-width progressively, the continuous spectrum is excluded from the recorded image of the incident line to a corresponding extent, until finally when the slit is narrow enough to give the full resolving power of the instrument, only those scattered radiations are recorded in the position of the line due to the incident radiation which are inseparable from the latter by the spectroscope used. The depolarisation as measured in this limiting case may clearly be regarded as a physical constant for the liquid studied, provided the spectroscope used is powerful enough to make the separation of the discrete incident line from the continuous spectrum overlying it *effectively complete*.

Theoretical — Very early in the history of the subject, it was suggested by Raman and Krishnan (1928) that the continuous band which appears overlying the undisplaced lines in the spectrum of the scattered light owes its origin to the rotation of the molecules in the liquid. This view receives support from various considerations and especially from the fact that the band is most conspicuous with molecules which have a high degree of optical anisotropy, *e.g.*, benzene or carbon disulphide. In view of the dense packing of the molecules in a liquid, the band could scarcely be expected to exhibit a discrete rotational structure or even the same general distribution of intensity as in the corresponding phenomenon observed with gases. This theory of the origin of the continuous band finds support in the observation by McLennan (1930) that liquid hydrogen exhibits discrete rotational lines instead of a continuous band. It is also substantiated by the investigations of Bhagavantam (1931), Trumphy (1933), Bhagavantam and Rao (1933) and of Weiler (1935), who have shown that in the rotational Raman spectrum of compressed gases, the discrete lines tend to be replaced by a continuous band with increasing pressures, and that the intensity-distribution in the same tends to approach that in a liquid. The most essential consequence of the Raman-Krishnan theory is however that the undisplaced lines in the spectrum should exhibit a depolarisation which is smaller than the depolarisation of the total scattering. If it be assumed

that the part of the scattering due to the anisotropy of the molecules is partitioned between the undisplaced line (Q-branch) and the continuous band (P and R branches) in some known proportion, *e.g.*, the proportion indicated by theory for the scattering by the same substance in the gaseous state, the depolarisation factor for the total scattering can be very simply calculated from the depolarisation factor for the undisplaced line, or *vice-versa*. If we assume, on the other hand, that the molecules in a liquid instead of being more or less free to rotate, are held rigidly in fixed but arbitrary orientations (which is not an unreasonable supposition for a highly viscous liquid or glass), the P and R branches of the scattering would disappear, and the entire scattered light would appear in the Q-branch. The depolarisation factor of the undisplaced line would then be considerably greater than on the assumption of freedom of rotation, and we have the further consequence that the depolarisation factor as determined spectrographically with a wide and a narrow slit respectively would not be sensibly different.

It will be clear from the foregoing review that studies of the state of polarisation of the scattered light by the Raman-Bhagavantam technique have an important bearing on the problem of the structure of liquids. It is the purpose of this paper critically to examine the earlier investigations in this field and to describe some observations and measurements showing that the "depolarisation of unmodified scattering" in a liquid is a definite physical constant depending on the chemical nature of the substance and its temperature.

2 Definition of "Unmodified Scattering"

It will be understood that when we refer to the undisplaced lines in the spectrum of the scattered light, we are ignoring the changes of frequency which are in the nature of Doppler displacements, these are so small that they would not be readily detectable with a prismatic spectroscope. It is known that when the incident light is so highly monochromatic as to be represented by a single sharp line in an interferometer pattern, the radiation after being transversely scattered in a liquid, *e.g.*, benzene, is modified by the thermal agitation into a band in which there are usually three recognisable components. In this triplet, the central component is in the undisplaced position of the incident radiation, while the two outer components are displaced by about 0.2 wave-number on either side. A prismatic spectrograph having a resolving power of as much as 100000 in the 4000 Å region of the spectrum would fail to resolve the triplet into its components and would thus present them together as a single line on the plate, at the same time, it would effectively exclude all the continuous radiations in the scattered light from the recorded image of this line, except such of it as actually falls within

the region of the triplet. A spectrograph of this resolving power would therefore enable the depolarisation of the aggregate radiation comprised within the triplet to be measured without sensible error. We may define the depolarisation as measured under these conditions as the "depolarisation of unmodified scattering" by the liquid. Instruments of a smaller resolving power, e.g., 50000, would naturally allow part of the continuous spectrum lying outside the triplet to be superposed upon the image of the latter. The error in the measurement of depolarisation thus resulting would depend on the relative intensity of the radiations composing the triplet and of the continuous spectrum outside it, and also on the actual value of the depolarisation itself. So long as the latter is not too small and provided the continuous spectrum is of sufficiently low intensity, the error involved in the use of an instrument of inadequate resolving power would not be serious. The effect of opening the slit of a spectrograph beyond a certain permissible limit is to reduce its resolving power. It should therefore be possible by extrapolation to make at least a rough estimate of the error involved in using an instrument of inadequate power for the measurement of depolarisation in any particular case by the method of variable slit-width.

3 Review of Earlier Work

The depolarisation of unmodified scattering was measured for a series of liquids at the suggestion of Sir C. V. Raman by S. P. Ranganadham (1932, 1933). In his first set of experiments, Ranganadham (1932) used a small instrument (a wave-length spectrometer by Hilger) with a resolving power of about 5000, and the results obtained with its aid showed only a moderate difference between the wide and the narrow slit depolarisation values. A little later, Ranganadham (1933) repeated the work, using an improved photometric technique and with a larger instrument (a Fuess glass spectrograph) with a resolving power about 25,000, he also used the finest possible slits for determining the depolarisation of the unmodified scattering. In this work, much greater differences were observed between the wide and narrow slit values for the depolarisation. He found also that when the "narrow" slits used with the Fuess instrument were not set sufficiently fine, the values obtained with the instrument of less resolving power could be reproduced. The importance of using an instrument of adequate power was very clearly realised and set out in Ranganadham's M. Sc. thesis of 1933 which is deposited in the Madras University Library, but has remained unpublished. It appears therefore desirable to reproduce below the following data extracted from this thesis. The figures shown in all the columns indicate the depolarisation factor of the transversely scattered light, the incident light being unpolarised.

TABLE I

Depolarisation with Narrow and Broad Slits
(Determined by S P Ranganadham in 1933)

Liquids	Hilger Spectrograph Resolving power ~ 5000		Fuess Spectrograph Resolving power ~ 25000	
	Narrow slit	Broad slit	Narrow slit	Broad slit
1 Benzene .	0 34	0 425	0 20	0 41
2 Carbon disulphide .	0 50	0 65	0 33	0 64
3 Carbon tetrachloride	0 06	0 07	0 012	0 039
4 Toluene			0 22	0 49
5 Acetone	0 18	0 25	0 09	0 21
6 Diethyl ether .	0 055	0 08	.	.
7. Ethyl alcohol .			0 03	0 055
8 N Propyl alcohol	.		0 03	0 070
9 Isopropyl alcohol . .			0 04	0 068
10 Butyl alcohol .	0 08	0 09	0 06	0 110
11 Isobutyl alcohol	0 055	0 075	0 059	0 125
12 Amyl alcohol .	0 065	0 080	0 070	0 12
13 Propyl acetate . .	0 160	0 20	.	..
14 Chloroform	0 145	0 21	0 06	0 19
15 Formic acid . .	0 49	0 52	0 53	0 55
16 Acetic acid .	0 385	0 40	0 395	0 41
17 Butyric acid . .			0 25	0 35
18 Salol . . .	0 75	0 75		.

It will be noticed from the figures in the table that in the case of many common liquids such as benzene, toluene, acetone and carbon disulphide, the depolarisation of the unmodified scattering as determined with the Fuess spectrograph is strikingly less than that of total scattering. In the case of highly associated liquids such as the fatty acids, on the other hand, the difference is much less striking, and in the case of a very viscous liquid such as salol, there is no noticeable difference between the two values.

The depolarisation values for four liquids (benzene, carbon disulphide, acetic acid and sulphur dioxide) determined with a series of slit-widths ranging from $2500\ \mu$ to $25\ \mu$ are recorded by Rousset in his doctorate thesis (Paris, 1935). The instrument used in this work was a two-prism glass spectrograph having a dispersion of $20\ \text{\AA}$ per millimeter in the region of $4358\ \text{\AA}$ and a theoretical resolving power of about 50,000. The focal length of the collimator was 67 cm and that of the camera, 47 cm. An extract from Table VIII of Rousset's thesis giving his data for the four liquids is reproduced below as Table II. In Fig 5 of his thesis, Rousset has given graphs of his depolarisation data as a function of slit-width from which it would appear that the form of the curves for these four liquids is rather varied. The graphs for acetic acid and sulphur dioxide show points of inflexion as they approach the axis of zero slit-widths, while the curves for benzene and carbon disulphide go steeply downwards in such manner as to suggest that the depolarisation of the unmodified scattering is very small if not actually zero.

TABLE II
Depolarisation with Varying Slit-Width
Rousset (1935)
Resolving Power of Spectrograph ~ 50000

Liquid	Slit Width in μ						
	2500	1000	500	200	100	50	25
Benzene	0.44	0.41	0.39	0.33	0.29	0.20	≈ 0.13
Carbon disulphide	0.62	0.60	0.58	0.53	0.48	0.41	≈ 0.33
Acetic acid	0.39	0.39	0.37	0.35	0.32	0.30	≈ 0.29
Sulphur dioxide	0.29	0.29	0.28	0.25	0.21	0.18	≈ 0.17

Rousset's graphs are however on a small scale and the actual measured values are not plotted therein. The reader of the thesis is unable therefore to judge for himself to what extent the graphs are a representation of the actual observations and to what extent they represent conjectural extrapolations. Accordingly, the present author has plotted out all the observations of Rousset for the four liquids on a large scale, and the same is reproduced as Fig 1 below in which for convenience of reproduction, the portion of the graph for slit-widths greater than $1000\ \mu$ has been omitted. Rousset remarks in his paper "Les valeurs de ρ pour les fentes de $25\ \mu$ sont obtenues après une comparaison grossière des densités au microscope", and indicates in his Table VIII that they are not to be given the same weight as the observations

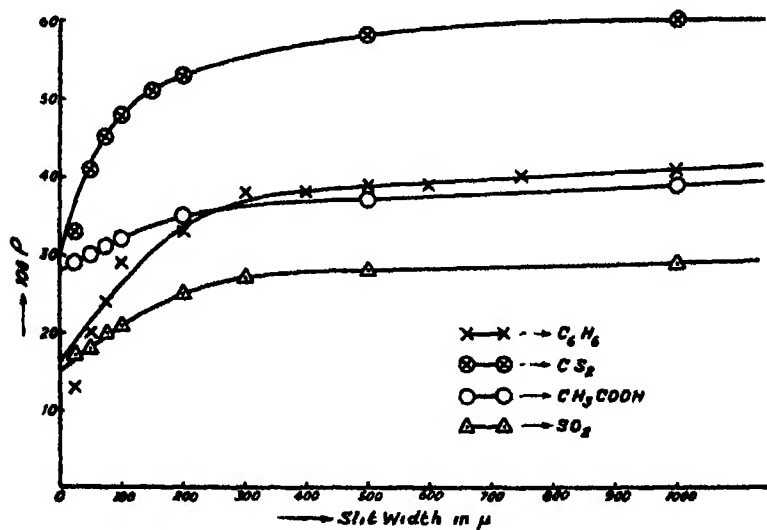


FIG 1

Rousset's values of depolarisation with varying slit-widths

with wider slits. It will be seen that all the measurements with acetic acid fall on a smooth curve which becomes a horizontal straight line for large slit-widths, and bends round and cuts the vertical axis of the graph sharply at an angle. The observed values for sulphur dioxide also fit tolerably well into a smooth graph of the same general form. All the observations for carbon disulphide fit perfectly into a curve of the same general form (though naturally higher and steeper) except the doubtful observation for $25\ \mu$ which falls a little out of the graph. The observations for benzene, though most numerous, are curiously enough, the least regular. A graph of the same general form as for the three other liquids, can, however, be drawn which

passes pretty evenly through the observed points, except however the doubtful observation for $25\ \mu$ which falls out of the graph. The curve for benzene is less steep than for carbon disulphide but steeper than for the other two liquids.

A re-examination of Rousset's own data thus makes it highly probable that the graphs for all the four liquids studied by him are of the same general form though of different height and steepness, meeting the vertical axis sharply at an angle and giving finite values for the depolarisation with the narrowest slits as shown below

Benzene, $\rho_0 = 0.16$, carbon disulphide, $\rho_0 = 0.30$

Acetic acid, $\rho = 0.28$, sulphur dioxide, $\rho = 0.15$

If we exclude the observations with the $25\ \mu$ slit which according to Rousset himself are not entitled to the same weight as the values with wider slits, his data clearly offer no basis for the suggestion that the depolarisation of the unmodified scattering in benzene and carbon disulphide is very small or zero. If his values for the $25\ \mu$ slit had been 0.185 instead of 0.13 for benzene, and 0.36 instead of 0.33 for carbon disulphide, they would have fitted perfectly into our present graph. To assume that errors of the magnitude indicated were not possible in what was admittedly "*une comparaison grossière*" and to base upon them an extrapolation having no observational support does not seem to be a justifiable procedure. A conclusion of such fundamental importance as that suggested by Rousset could only be accepted on the clearest experimental evidence, and that its truth is highly improbable is indicated by his own data. As we shall see later, it is definitely contradicted by the experimental evidence offered in the present paper.

4 Some General Observations

The relative intensity with which monochromatic light and a continuous spectrum superposed upon it are recorded by a spectrograph depends on the resolving power of the instrument and, in fact increases *pari passu* with the "purity" of the spectrum given by the instrument. With an instrument of low power, the continuous spectrum appears relatively brighter, and when, as in the present case, its maximum intensity coincides with the monochromatic line itself, the line and continuous spectrum tend to fuse into each other on the photographic plate and to convey the impression that the line has suffered an "*élargissement*" or widening. This effect would naturally be aggravated by the photographic broadening due to over-exposure of the intense image of the monochromatic radiation, and the net result would be to convey an incorrect impression of the real nature of the phenomenon encountered in the scattering of monochromatic light by liquids. *Actually, there is no*

"elargissement" or widening of the incident radiation, when a spectrograph of sufficient power is used, it is observed that the undisplaced line in the scattered light has precisely the same degree of sharpness as in the incident light. This is most evident with an instrument in which a large linear dispersion is combined with a great resolving power, as the effect of photographic broadening is then minimised. If a photograph is taken of the spectrum of scattered light with such an instrument, and the negative is examined against a strong light, it will be seen that the undisplaced lines appear with undiminished sharpness superposed on a continuous spectrum which has its maximum intensity at the line itself. Fig 1 (Plate) represents the 4358 group of lines of the mercury arc in the transverse scattering by benzene, recorded with a three-meter-focus glass spectrograph constructed by Dr C S Venkateswaran with optical parts by Hilger. In the reproduction of this picture which was taken as a test of the instrument by Dr Venkateswaran with an exposure of 48 hours and without any special precautions for maintaining constancy of temperature, the weaker lines which have not suffered from over-exposure appear defined with hair-like sharpness.

If the depolarisation of the undisplaced line in the transverse scattering by benzene were very small or zero as suggested by Rousset, then the incident lines should completely disappear and be lost in the continuous background if the scattered light were analysed with a double-image prism and the horizontal component alone were recorded. The experiment is readily tried and it is found that the facts afford no support to Rousset's conclusion. Actually, the lines are seen in the vertical and horizontal components (Fig 2 in the plate) with entirely comparable clearness and definition. Though the lines in the horizontal component are weaker, their intensity is far from being negligible, and in fact, is a very considerable fraction of the intensity in the vertical component. The visibility of the lines in the horizontal component against the continuous background is not notably inferior to the visibility of the lines in the vertical component. The greater relative intensity of the continuous background in the horizontal components however affects the appearance of the lines as recorded on a photograph and seen under a microscope or in a microphotometer record. The reason for this will be clear from Fig 2 (a), (b) and (c) below, in (a) we have the vertical component alone, in (b) the horizontal component alone and in (c), the two together. As the result of photographic spreading, the vertical component in (a) will, when reduced to the same intensity as the horizontal component in (b) by a suitable device *e.g.*, by a nicol following the double-image prism, will appear sharper than the latter. The magnitude of this effect will depend on the degree of depolarisation of the undisplaced line and its intensity relatively to the continuous

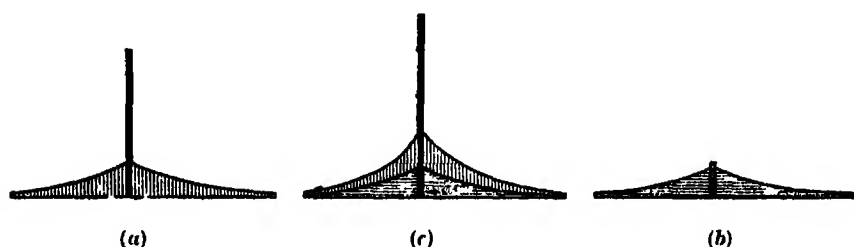


FIG. 2

Intensities of modified and unmodified radiations

spectrum Microphotometric records of the undisplaced line in the horizontal and vertical components taken with a Hilger E 349 spectrograph and slit only 10μ wide are reproduced in Fig 3 and Fig 4 in the plate Fig 3 refers to phenol and it will be seen that the horizontal and vertical components

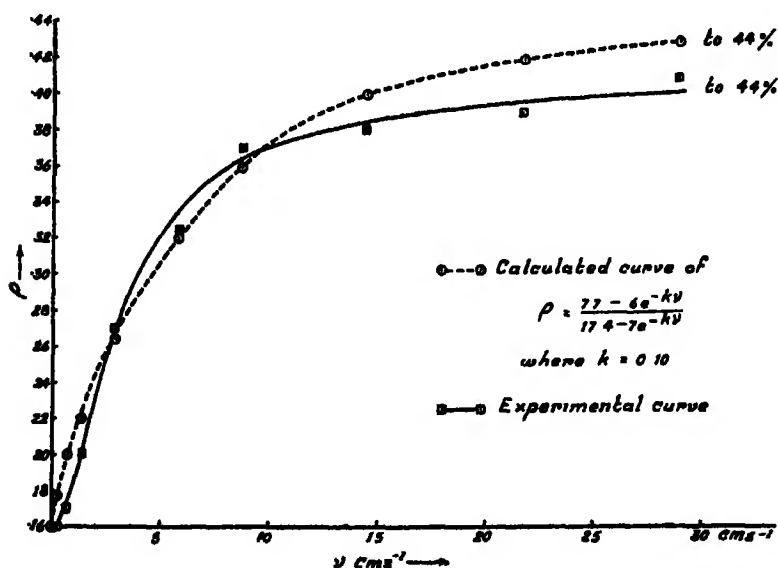


FIG. 3

Depolarisation factors in benzene with different slit-widths.

are of equal sharpness Fig 4 refers to benzene, and the vertical component appears somewhat sharper than the horizontal one, for the reason already explained.

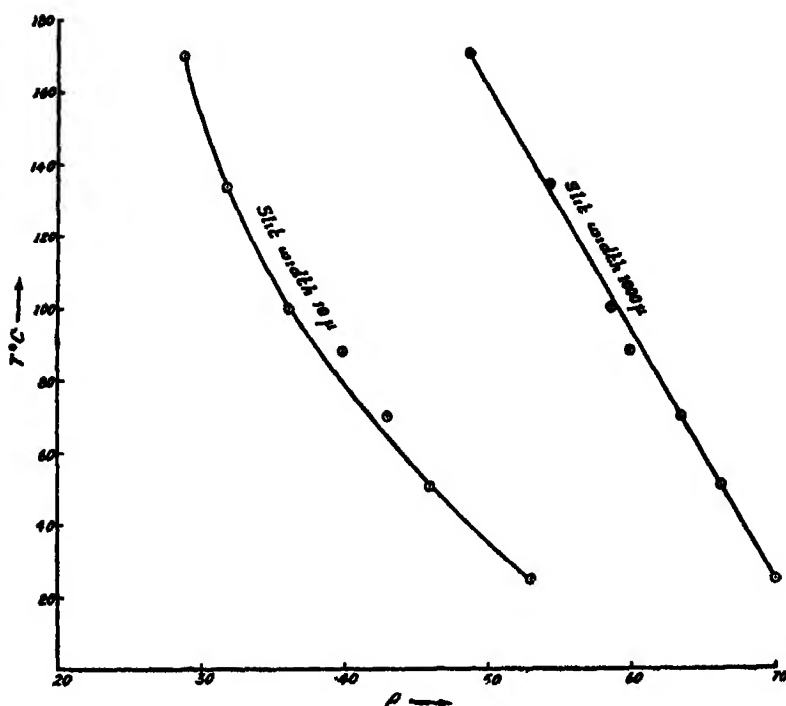


FIG. 4.

Variation of depolarisation (wide and narrow slits) in phenol with temperature

5 Method for Exact Measurements.

To remove all possible doubt on the issues now under discussion, it is clearly necessary that the measurements of depolarisation should be made with a spectrograph of the largest possible resolving power and dispersion, and that observations should be secured covering a range of slit-widths up to the very finest possible, thus enabling the whole course of the curve to be traced from actual observations and not by extrapolation. Both Ranganadham and Rousset used the methods of photographic photometry for making their determinations. In Ranganadham's first series of measurements and in Rousset's work, Schwarzschild's formula connecting the depth of blackening and the time of exposure was used to determine the ratio of the intensity of the vertical and horizontal components. In Ranganadham's second series of measurements, the comparison was based on the method of intensity marks. When the images under comparison are extremely fine lines on the plate of width comparable with that of the grains of the emulsion,

a method of measurement independent of the laws of photographic action and which merely uses the plate as a detector seems preferable

In the present investigation, the spectrograph used was a large Littrow glass spectrograph by Hilger (E 349) of aperture $F/7$, the diameter of the camera objective being 127 mm. The prism system of dense flint glass is equivalent to three 60° prisms of 15.2 cms face and 11.7 cm high. The dispersion is 11 Å per mm in the 4358 region of the spectrum. A mercury arc lamp was the source and the lens which condensed the light from it was screened off by an aperture 3 cm square. The lens itself was 8 cm in diameter and 24 cm distant from the tube. The liquid under study was contained in a cylindrical glass tube with a fused-on flat end, and the scattered light was taken from an aperture 0.2 cm wide at the centre of the latter. Thus light was condensed on the spectrographic slit by a convex lens of diameter 3.5 cm (focal length 11 cm) which was 26 cm distant from the slit and 18 cm from the tube. A double-image prism of quartz was mounted on the same stand as the lens and faced the slit of the spectrograph. The method adopted for measuring ρ was different from that of previous workers. A nicol was interposed in the path of the scattered beam after it had traversed the double-image prism and before it entered the slit of the spectrograph. Successive exposures were given with the nicol turned round 1° at a time, until the relative intensity of the two images recorded showed a reversal, that is, till the weaker image became the stronger and *vice versa*. If α be the orientation of the nicol, the depolarisation factor is given by the usual formula $\rho = \tan^2 \alpha$. The method, though tedious, has the merit of being entirely reliable and applicable to the finest slit-widths.

6 Results

Hilger E 349 Glass Spectrograph, Resolving Power ~ 75000

A Variation of Depolarisation with Slit-width in benzene

Slit-width in μ	1500	1000	750	500	300	200	100
Depolarisation factor	. 0.44	0.41	0.39	0.38	0.37	0.32	0.27
Slit-width in μ	. 50	25	10				
Depolarisation factor	.. 0.20	0.17	0.16				

B Depolarisation with wide and narrow slits in different liquids at room temperature, 20° C.

Liquid	Wide slit	Narrow slit (10 μ)
Benzene	0 44	0 16
Phenol	0 70	0 53
Benzophenone	0 75	0 66
Glycerine . .	0 33	0 30

C Variation of ρ with temperature in Phenol

Temperature	175° C	134° C	100° C	84° C	65° C	45° C	23° C
Slit-width 1000 μ	0 49	0 55	0 59	0 64	0 60	0 66	0 70
Slit-width 10 μ	0 29	0 32	0 36	0 40	0 43	0 46	0 53

7 Interpretation of the Results

The experimental results for benzene given above have been represented graphically in Fig 3. The ordinates are the observed depolarisation factors, and the abscissæ are the half-width of the image of the slit as it appears on the photographic plate expressed in wave-numbers, in other words, the actual range of the continuous spectrum on either side which appears superposed on the central undisplaced line. The graph also shows the values calculated from the empirical formula

$$\rho = \frac{7}{17} \frac{7 - 6e^{-K\nu}}{4 - 7e^{-K\nu}} \quad (\text{Benzene})$$

where ν is the half-width of the slit expressed in wave-numbers and $K = 0.10$. For $\nu = 0$, that is, for a very fine slit, ρ becomes 0.16, while for large values of ν , ρ becomes 0.44. This empirical formula can be derived theoretically, if the distribution of intensity in the continuous spectrum is assumed to be proportional to $e^{-K\nu}$, in other words, that it has a finite maximum intensity at the position of the undisplaced line and falls off exponentially with increasing wave-number shift from it. The asymmetry in the intensity of the continuous spectrum on the two sides of the undisplaced line which

develops with increasing ν is rather small compared with the rapid fall in the intensity of the continuous spectrum which occurs simultaneously, it is therefore neglected in the derivation of the formula for the sake of simplicity, though it is easily possible to take account of it as well. The depolarisation factor of the continuous spectrum is taken as $6/7$, and these integers, it will be seen, appear respectively in the numerator and denominator of the formula. The agreement between the observed values of ρ and those given by the empirical formula though fair, is not all that could be desired. A formula of the general type

$$\rho = \frac{x - 6}{y - 7} \frac{c^{\nu}}{c^{-\bar{\nu}}}$$

has been tested out and is found to fit Rousset's data (Fig. 1 above) tolerably well. The constants found are

Benzene	$x = 7.7$	$y = 17.4$	$K = 0.09$
Carbon disulphide	$x = 7.6$	$y = 12.2$	$K = 0.12$
Acetic acid	$x = 14.3$	$y = 36.7$	$K = 0.10$
Sulphur dioxide	$x = 10.3$	$y = 35.4$	$K = 0.13$

The observations recorded above for the viscous liquids benzophenone and glycerine show very clearly that the intensity of the continuous spectrum relatively to that of the undisplaced line is very small with these liquids, and also that the depolarisation of unmodified scattering is correspondingly high in these cases. These facts fit in very well with the theoretical considerations referred to in the introductory part of the paper. The case of phenol is particularly interesting, as it evidently stands midway between the class of liquids including benzene and carbon disulphide in which the depolarisations of the total scattering and of the unmodified scattering differ widely, and the class of viscous liquids including benzophenone and glycerine in which they differ very little. It might reasonably be anticipated that with rise of temperature, phenol would tend to behave more like the liquids in the former class. The relation between ρ and the temperature for the largest and the smallest slit widths respectively for phenol has been plotted in Fig. 4, and it will be seen that this anticipation is at least partially fulfilled. The experiment clearly indicates that we may expect the depolarisation of unmodified scattering to be markedly a function of temperature in all liquids, and that it would differ markedly from the depolarisation of total scattering at higher temperatures, even with those liquids for which the difference is ordinarily small.

8 Summary

The investigations of Ranganadham and of Rousset have been critically examined, and it has been shown that, contrary to the latter's conclusion, normal liquids such as benzene and carbon disulphide show a definite depolarisation of the unmodified scattering which is notably smaller than the depolarisation of the total scattering. From Rousset's data for the four liquids studied by him, the following results have been derived

	Unmodified	Total
Benzene	0 16	0 44
Carbon disulphide	0 30	0 62
Acetic acid	0 28	0 39
Sulphur dioxide	0 15	0 29

The value for benzene deduced above is confirmed by a thorough re-investigation with a spectrograph of adequate power and an exact experimental technique. Viscous liquids such as phenol, benzophenone and glycerine give relatively smaller differences between the depolarisations of unmodified scattering and of total scattering at room temperatures as shown below

	Unmodified	Total
Phenol	0 53	0 70
Benzophenone	0 66	0 75
Glycerine	0 30	0 33

The depolarisation of unmodified scattering diminishes with rising temperature, and the investigation with phenol at temperatures ranging from 23° C to 175° C shows that it tends to differ more markedly from the depolarisation of total scattering at the higher temperatures than at the lower

In conclusion, the author wishes to express his grateful thanks to Sir C V Raman at whose suggestion this investigation was undertaken for his sustained interest in its progress

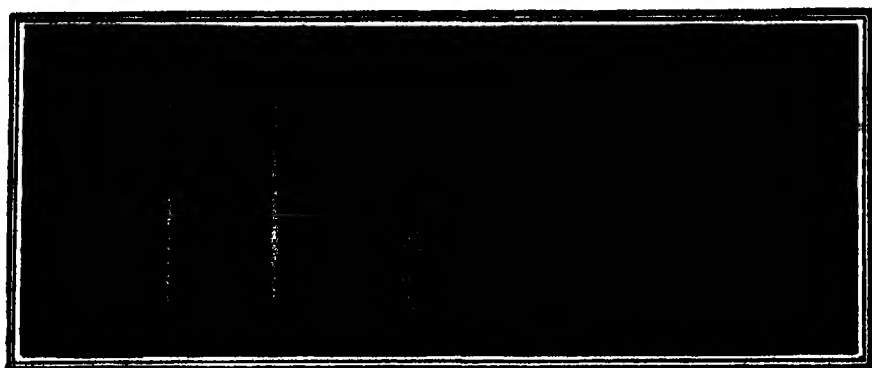
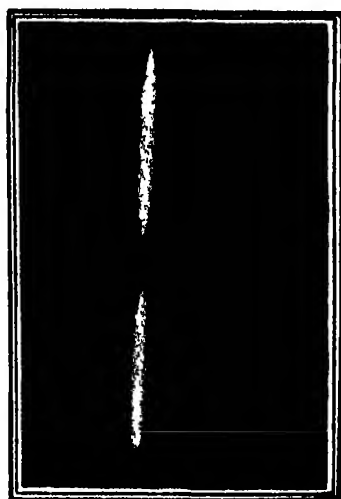


FIG 1 Wing in Benzene

FIG 2
Transverse Scattering
in Benzene



Vertical
Component

Horizontal
Component

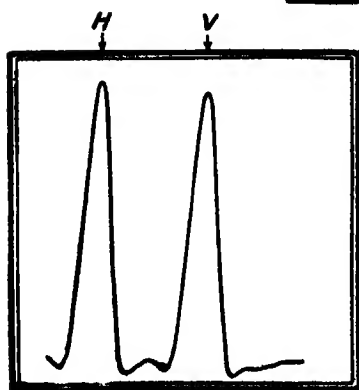


FIG 3 Phenol

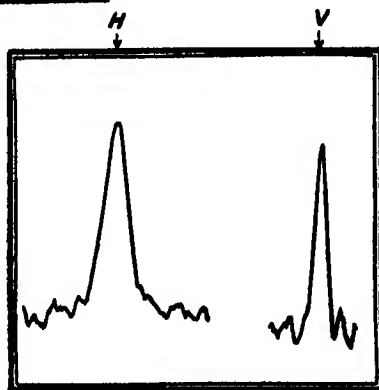


FIG 4 Benzene

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THE RAMAN EFFECT AND MULTIPLE SCATTERING OF LIGHT.

BY A KASTLER

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WHEN a homogeneous and chemically defined substance is irradiated with monochromatic light, part of the energy of light is subtracted from the incidental pencil and diffused by the molecules. The most important part of the scattered light is that possessing the same frequency as the incidental radiation (Rayleigh line), but a definite fraction of the energy of light which is scattered by the molecules, undergoes a change of frequency (Raman effect). In expressing by r the probability for a photon to change its frequency during the mechanism of scattering, the probability that the scattering occurs without any change of frequency will be $(1 - r)$. Disregarding terms like $\frac{\Delta \nu}{\nu_0} = \frac{r}{N}$ (ν_0 = incidental frequency, $\Delta \nu$ = Raman frequency), the ratio $\frac{r}{1 - r}$ can be identified by the number measuring the ratio of the sum of the intensities of the Raman lines and the intensity of the Rayleigh line*. This ratio amounts to 10^{-3} for gases, 10^{-2} to 10^{-1} for liquids and it may reach the value of $\frac{1}{2}$ for crystals†. The ratio r has a specific fixed value for a determined substance, taken under definite conditions of pressure and temperature.

The object of the present article is to study the distribution of scattered photons in the field of frequencies, after several successive scatterings

* P being the number of photons contributing to the Rayleigh line and p the number of photons of a Raman line, the ratio r is defined by

$$\frac{r}{1 - r} = \frac{\sum p}{P}.$$

The ratio of energies is $j = \frac{r'}{1 - r'} = \frac{\sum p h \nu}{P h \nu_0} = \frac{\sum p (\nu_0 - \Delta \nu)}{P \nu_0}$. It is slightly different

† For the vibration line of hydrogen (its rotation structure included) we have according to Mrowka

$$j = \frac{r'}{1 - r'} = \frac{\text{Raman intensity}}{\text{Rayleigh intensity}} \approx 3 \cdot 10^{-3} \quad (\text{Zeitschr f Physik, 1933, 84, 448})$$

For liquids, the factor j measured by P. Daure (see Kohlrausch, *Smekal Raman Effect*, I, p. 104) is included between 0,016 (benzene) and 0,10 (C_6H_6). Finally, for crystals, the factor j may be very great on account of the diminution of fluctuations. Landsberg-Mandelstamm have measured $j = 0,28$ (to 0,38) for the Raman line $\Delta \nu = 465$ of quartz (Kohlrausch, p. 102).

In order to simplify the question and to release the essential results, we shall render the problem schematic by means of the following hypothesis. It is supposed that the substance has one single Raman line of which the frequency $(N - n)$ is little different from the exciting frequency N †. What will be the distribution of the photons in the field of the frequencies after m successive scatterings?

After the first scattering, there will be

Exciting frequency	Scattered frequency	Number of photons
$N \swarrow$ Rayleigh effect \rightarrow	N	$(1 - r)$
$N \searrow$ Raman effect \rightarrow	$N - n$	r

After the second scattering, there will be

Exciting frequency	Number of photons	Effect	Scattered frequency	Number of photons	Total
N	$(1 - r)$	{ Rayleigh Raman	N $\{ N - n$	$(1 - r)^2$ $(1 - r) r$	$(1 - r)^2$ $2(1 - r) r$
$N - n$	r	{ Rayleigh Raman	$\{ N - n$ $N - 2n$	$r(1 - r)$ r^2	r^2

After the first scattering, the proportion will be indeed $(1 - r)$ photons of frequency N (Rayleigh effect) against r photons of frequency $(N - n)$ (Raman effect).

If this light undergoes a second scattering on an identical medium, the photons of frequency N will give scattered photons of frequency N and $(N - n)$, and the photons of frequency $(N - n)$ will give by scattering photons of frequency $(N - n)$ and $(N - 2n)$.

After two successive scatterings, the scattered light will consequently be distributed on three different frequencies, N , $N - n$ and $N - 2n$, the proportion of photons between these three frequencies being $P_0 = (1 - r)^2$, $P_1 = 2(1 - r) r$, $P_2 = r^2$.

† In this case we can disregard in first approximation the variation of the scattering power with the frequency. Strictly, it would be necessary to take into account the factor $\left(\frac{N - n}{n}\right)^4$.

After three successive scatterings, there will be .

Existing frequency	Number of photons	Effect	Scattered frequency	Number of photons	Total
N	$(1-r)^2$	{ Rayleigh Raman	N	$(1-r)^2$	$(1-r)^2$
N - n	$2(1-r)r$	{ Rayleigh Raman	$\begin{cases} N-n \\ N-n \end{cases}$	$\begin{cases} (1-r)^2 r \\ 2(1-r)^2 r \end{cases}$	$3(1-r)^2 r$
N - 2n	r^2	{ Rayleigh Raman	$\begin{cases} N-2n \\ N-2n \\ N-3n \end{cases}$	$\begin{cases} 2(1-r)r^2 \\ r^2(1-r) \\ r^2 \end{cases}$	$3(1-r)r^2$

It is unnecessary to make any comment on this table and to pursue this computation step by step

The general rule is easily to be guessed Putting down $(1-r) = A$ and $r = B$, the relative numbers P_i of photons of frequency $(N - in)$ after m successive scatterings, are given by the successive terms of the development of the binomial $(A + B)^m$

Thus

$$P_0 = A^m = (1-r)^m \text{ photons of frequency } N$$

$$P_1 = mA^{m-1}B = m(1-r)^{m-1} \cdot r \text{ photons of frequency } (N - n)$$

$$P_2 = \frac{m(m-1)}{2} A^{m-2} B^2 = \frac{m(m-1)}{2} (1-r)^{m-2} \cdot r^2 \text{ photons of frequency } (N - 2n)$$

$$P_i = \frac{m(m-1) \cdots (m-i+1)}{i!} (1-r)^{m-i} \cdot r^i \text{ photons of frequency } (N - in)$$

$$P_m = B^m = r^m \text{ photons of frequency } (N - m \cdot n)$$

$$\text{We have always by definition } \sum_m P_i = 1$$

The result can be expressed as follows —

After having gone through m successive scatterings the scattered light is distributed on m different frequencies going from N to $(N - mn)$ and forming an arithmetical progression When m increases, the proportion P_0 of unchanged photons decreases in geometrical progression and the proportion of modified photons becomes more and more important In the beginning P_1 increases most rapidly but attains a maximum and decreases to give way to P_2 , etc. . . At the same time, the value of the successive maxima decreases the photons spread on a more and more extensive "spectre".

We are going to specify the pace of this phenomenon of "frequency degradation", in case r is very little before the unity. In such a case it is possible to introduce the argument $x = m \cdot r$ and to assimilate it to a continuous argument

It is possible to write down

$$\begin{aligned} P_0 &= (1 - r)^m (1 - r)^{\frac{1}{r} x} \approx e^{-x} \\ P_1 &= x (1 - r)^{m-1} \approx x e^{-x} \\ P_i &\approx \frac{x^i}{i!} e^{-x} \end{aligned}$$

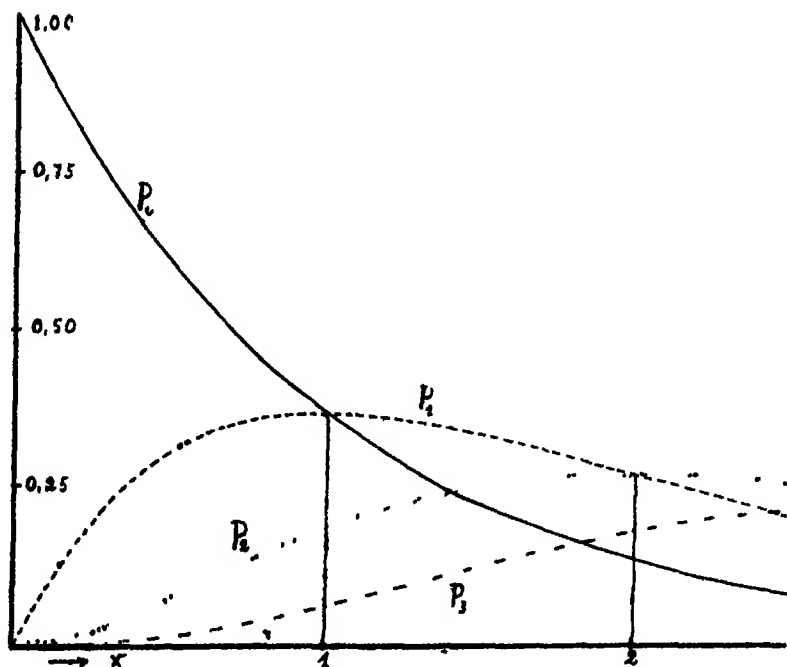


FIG. 1

The maximum of P_1 will occur for

$$\frac{dP_1}{dx} = e^{-x} \cdot x^{i-1} \cdot [i - x] = e^{-x} x^{i-1} \cdot \left[\frac{i}{x} - 1 \right] = 0$$

that means for $x = i$, namely $m = i \cdot \frac{1}{r}$

It has for ordinate

$$(P_i) \text{ max.} = \frac{e^{-i} \cdot i^i}{i!} = \frac{e^{-i} \cdot i^{i-1}}{(i-1)!} = P_{i-1}$$

There are tables giving the numerical values of the functions P_r .¹ Fig 1 represents graphically the functions of P_0 to P_8 for x from 0 to 2.5

It will be seen that the intensity of the Rayleigh line prevails up to $x = 1$ ($m = \frac{1}{r}$). For $x = 1$, we have $P_0 = P_1 = 1/e = 0.368$. Between $X = 1$ and $X = 2$ the principal Raman line of frequency $(N - n)$ is most intense, then the maximum of relative intensity passes to the "secondary" Raman lines of frequency $N - 2n, N - 3n$, etc. The energy of light degrades and at the same time it is spreading. Fig 2 shows this spreading

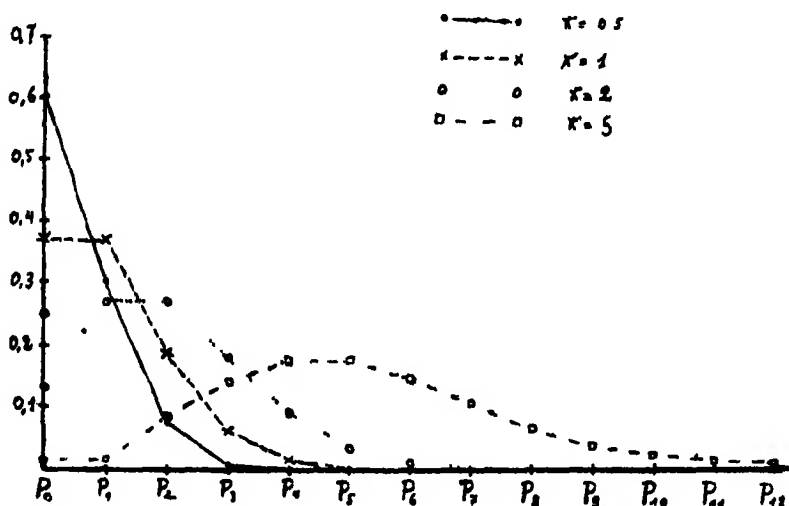


FIG 2.

Each curve corresponds to a specific value of x and shows how the number of photons brought in ordinate is distributed amongst the various frequencies P_0, P_1 , etc

When r is not negligible before the unity, the reasoning becomes a little more complicated, but the general aspect remains the same

Thus for quartz r is near to $\frac{1}{2}$. Four successive scatterings will be sufficient to render the Raman line just as important as the Rayleigh line, and nearly 30% of the quaternary scattering will belong to the lines of frequency $(N - 2n)$ and upwards

In order to observe this phenomenon of the "stepwise degradation" of the photons, one could establish a stepwise mounting in order to realize

¹ Pearson, *Tables for Statisticians and Biometrists*, Part 1, 3rd ed., p 113

the successive scattering of the light, by means of condenser-lenses (Fig 3) In this way, it is possible to observe in its pure state the light at each stage of scattering primary, secondary, tertiary scattering, etc

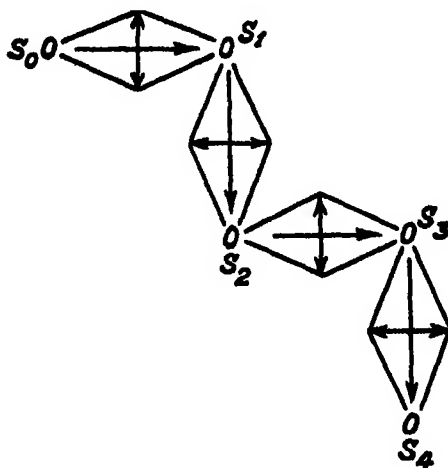


FIG 3

If it were only desired to observe the superposition of various effects, one could be satisfied by sending back the greater part of the scattered light a great number of times, in the first scattering medium This is taking place practically in the mounting of Wood, with a cylindrical reflector surrounding the source and the scattering medium, and thereby "imprisoning" the light (Fig 4) It would be interesting to investigate whether this mounting

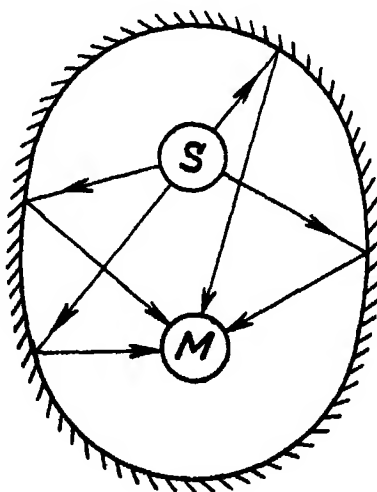


FIG 4.

is not particularly efficacious to render visible the lines of secondary scattering (of frequency $N-2n$, etc) The measurements of j which were effected with this mounting are doubtless little trustworthy and are too high in a systematic way

Another method for observing the effect of multiple scattering consists in analysing the light of a source which has filtered through a very thick scattering layer of an uninterrupted medium (a reflecting tube of several hundred yards length, containing a liquid or a thick stratum of glacier) In such a case, there is reason to modify the preceding theory, because the different steps of scattering do not appear by discontinued bounds, but they get entangled in a continuous manner according to an exponential law of absorption. For this reason it will be useful to take up again Milne's theory of scattering,² incorporating the Raman effect in the same The degradation of the quanta of light by multiple molecular scattering plays doubtless a less important part in the phenomena on our scale, but it might intervene in the phenomena of scattering on the astronomical scale, where the thickness of the scattering medium may become great in comparison with the "average free path" of the photons The spectral composition of a radiation which is filtered through a thick layer of scattering matter can be, in such case, entirely different from that of an incidental radiation, and it could be asked whether certain unknown radiations, which were observed in astrophysics, could not be explained as due to degradation of frequency caused by a multiple scattering

² E. A. Milne, *Journ Lond. Math. Soc.*, 1926, 1, 1.

STUDIEN ZUM RAMAN-EFFEKT.

Mitteilung XCIV Tetrolsäure und Ester.

VON O BALLAUS

(181. Mitteilung aus dem physikalischen Institut der Technischen Hochschule Graz)

(Mit 1 Figur im Text.)

Die im hiesigen Institut begonnene spektroskopische Untersuchung der Acetylen-carbonsäuren wurde fortgesetzt. *Sabathy*¹ berichtete über die Propiolsäure $\text{HC} \equiv \text{C} \cdot \text{COOH}$ und ihre Ester, die Raman-Spektren der nächsten homologen Säure, der Tetrolsäure $\text{H}_3\text{C} \cdot \text{C} \equiv \text{C} \cdot \text{COOH}$, und ihrer Ester sind der Gegenstand der vorliegenden Mitteilung.

1 Die Darstellung der Substanzen

Die Tetrolsäure wurde nach der Vorschrift *Kahlbaum's*² aus den Chlorcrotonsäuren und deren Aethylestern, die ihrerseits als Gemisch aus Acetessigester und PCl_5 gewonnen wurden, durch Entzug von HCl mittels KOH in stark verdünntem Alkohol dargestellt. Zur Reinigung wurde die Säure bei vermindertem Druck destilliert und zweimal im Hochvakuum sublimiert (0,02 mm Druck, 80–90° Temperatur des Luftbades). Der Aethylester wurde nach der Vorschrift von *Feist*³ durch direkte Veresterung mit Alkohol und Schwefelsäure gewonnen, Reinigung durch zweimalige Fraktionierung bei vermindertem Druck. Nach derselben Methode wurde der in der Literatur anscheinend noch nicht beschriebene Methylester dargestellt. Für die 3 Substanzen gelten die folgenden Konstanten:

	Säure	Methylester	Aethylester
Literatur	Kp_{18} 100°, Fp 76°		Kp_{752} 163–164°
Ich fand	Kp_{11} 97°, Fp 76°	Kp_{13} 54, 9–55, 1, Kp_{730} 148–149, 5°	Kp_{730} 160–161°

Von den von *Sabathy* angeführten unangenehmen Reizwirkungen der Propiolsäure auf Haut und Augen ist bei der Tetrolsäure fast nichts zu bemerken.

¹ R. Sabathy, *Ztschr. physikal. Chem.*, 1938, im Druck

² G. W. A. Kahlbaum, *Ber. Dtsch. chem. Ges.*, 1879, 12, 2338

³ F. Feist, *Liabig's Annal d. Chemie*, 1906, 345, 105

2 Die Raman-Spektren

Auch die bei der Propiolsäure und ihren niederen Estern bemerkte Lichtempfindlichkeit (rasche Verfärbung bei Belichtung ohne Filter) verschwindet in der Tetrolsäure und ihren Estern

Die *Tetrolsäure* wurde sowohl als Krystallpulver wie in wässriger Lösung spektroskopiert. Krystallpulver F_1 355, $t = 27$, F_1 356, $t = 96$, F_1 370, $t = 103$ Stunden, F_2 97, $t =$, in der Festkörper-Apparatur F_1 kommen die Hg-Linien g, f, e, in F_2 die Linien Hgk und Hg₁ als erregend zur Wirkung. Die wässrige Lösung (ebenso wie die flüssigen Ester) wurde in der "Normal-Apparatur" aufgenommen, Pl 2730, m F, Spalt 0,06, $t = 8$, Pl 2731, m F, Spalt 0,04, $t = 9$, Pl 2732, m F C (Abfilterung des Lichtes mit $\lambda < 4047$), Spalt 0,03, $t = 5$, Untergrund mittelstark, Spektrum gleichfalls Ergebnis

kryst	← nicht erfasster Bereich →			405 (1) (k, e),	594 (1) (k, e),	696 (0) (e),
Lösung	325 (3 b) (± e),	365 (4 b) (± e),	423 (00) (e),	498 (½) (e),	589 (½ b) (e),	709 (0) (e)
kryst	753 (1) (e),	785 (2) (k, e),	1026 (1 b) (e)	1079 (3) (k, e),	1254 (½) (k, e),	1373 (5) (k, e)
Lösung	755 (½) (e),	790 (½) (e),	1030 (0) (e),	1072 (½) (k, e),	1276 (1) (e),	1375 (3 b) (k, e)
kryst	1429 (0) (e),	1640 (6 b) (e),		2146 (1) (k, e),	2247 (8b) (k, i, f, e),	
Lösung	1427 (00) (e),	.	1692 (2 b) (e),		2242 (8 b) (k, i, e),	
kryst	2311 (0) (k),	2904 (0) (e),	2924 (6 h) (k, i, e),	2974 (½) (k)		
Lösung	2300 (0) (k),		2926 (7 h) (k, e),	2984 (1) (k, e)		

Tetrolsäure-methylester Pl 2715, m F, Sp 0,06, $t = 24$, Pl 2716, m F, Sp 0,06, $t = 8$, Pl 2721, m F C, Sp 0,04, $t = 9$ Untergrund mittel, Spektrum stark, Zahl der Streulinien $n = 53$ Ergebnis

$\Delta \nu = 295$ (1) (e), 340 (3) (k, e, c), 374 (8b) (± e, c), 475 (3) (k, i, e, c), 560 (3) (k, e, c), 753 (3) (k, e, c), 816 (6) (k, i, e, c), 944 (8b) (k, i, g, f, e), 1025 (1) (k, e), 1194 (1) (k, e), 1264 (5b) (k, e), 1377 (6b) (k, e), 1447 (4b) (k, e); 1710 ± 13 (8b) (f, e), 2243 (10b) (k, i, g, f, e), 2870 (2b) (k, e), 2925 (8b) (q, k, i, e), 2958 (4b) (q, p, k, e)

Tetrolsäure-äthylester Pl 2703, m F, Sp 0,06, $t = 14$, Pl 2704, m F C, Sp 0,06, $t = 9$, Pl 2705, m F C, Sp 0,04, $t = 9$, Untergrund mittel, Spektrum stark, $n = 42$ Ergebnis

$\Delta \nu = 214$ (½?) (e), 259 (½?) (e), 322 (3) (e), 370 (4) (± e, c); 572 (3) (± e, c), 752 (2) (k, e, c), 865 (5) (k, i, e), 1011 (2b) (k, f, e), 1114

(2b) (k, e), 1260 (3b) (k, e), 1302 (0) (k, e), 1380 (4b) (k, e), 1450 (3b) (k, e), 1705 ± 13 (7b) (f, e), 2166 (0') (k), 2239 (8b) (k, 1, e), 2927 (8) (k, 1, e), 2974 (5b) (q, p, k, e)

3 Diskussion der Ergebnisse

(a) Zuerst seien die C O- und C C-Frequenzen der Propiol- und Tetrol-Säuren und Ester zusammengestellt

		ω (C O)	ω (C C)
Säuren	$\begin{cases} \text{H C C CO OH (fl)} \\ \text{H}_3\text{C C C CO OH (kryst)} \end{cases}$	$\begin{matrix} 1670 \text{ (3 sb)} & 1715 \text{ (3b)} \\ 1640 \text{ (6 b)} \end{matrix}$	$\begin{matrix} 2122 \text{ (10b)} \\ 2247 \text{ (8b)} \end{matrix}$
Methylester	$\begin{cases} \text{H C C CO OCH}_3 \\ \text{H}_3\text{C C C CO OCH}_3 \end{cases}$	$\begin{matrix} 1714 \text{ (5b)} \\ 1710 \text{ (8b)} \end{matrix}$	$\begin{matrix} 2125 \text{ (12b)} \\ 2241 \text{ (10b)} \end{matrix}$
Aethylester	$\begin{cases} \text{H C C CO OC}_2\text{H}_5 \\ \text{H}_3\text{C C C CO OC}_2\text{H}_5 \end{cases}$	$\begin{matrix} 1708 \text{ (4b)} \\ 1705 \text{ (7b)} \end{matrix}$	$\begin{matrix} 2116 \text{ (12)} \\ 2239 \text{ (8b)} \end{matrix}$

Während in der flüssigen Propiolsäure, nach dem Auftreten zweier CO-Frequenzen zu schliessen, anscheinend sowohl dimere [mit ω (CO) = 1650] als monomere Moleküle [mit ω (CO) = 1715] vorhanden sind, findet man in der krystallisierten Tetrolsäure nur die, üblicher Weise den assoziierten Molekülen zugeschriebene erniedrigte Frequenz ω (CO) = 1640 deren Wert in Lösung auf 1692 ansteigt. Die CO-Frequenz in den Estern beider Säuren ist durch die Konjugation der Carboxalkylgruppe mit der C' C-dreifach Bindung vom Normalwert 1735 auf ~ 1710 erniedrigt.

Die Erklärung des im ersten Augenblick überraschenden Frequenz-Sprunges von 2121 nach 2243, der sich für die C C-Frequenz beim Uebergang von H C C CO OR nach R' C C CO OR einstellt, wurde schon von *Sabathy* gegeben. Im Falle des leichten Substituenten H gehört die sogenannte "C C Frequenz" zu einer andern Schwingungsform des Moleküles, als für den schweren Substituenten R'. Eine Anzahl ähnlicher Fälle behandelt *Burkard* in seiner Mitteilung "Durchrechnung einiger ausgewählter Molekülmodelle".

(b) In Figur 1 sind die Raman-Spektren der beiden homologen Substanz-Reihen zeichnerisch zusammengestellt. Die Bedeutung der in den Frequenzgebieten um 2900, 2200, 1700 liegenden Linien, die zu CH-, C C-, C O-Valenzschwingungen gehören, steht natürlich ausser Zweifel. Darüber kann man noch mit einiger Sicherheit die im Frequenzgebiet der CH-Deformations-Schwingungen auftretende starke Linie bei 1377 (ebenso wie in den

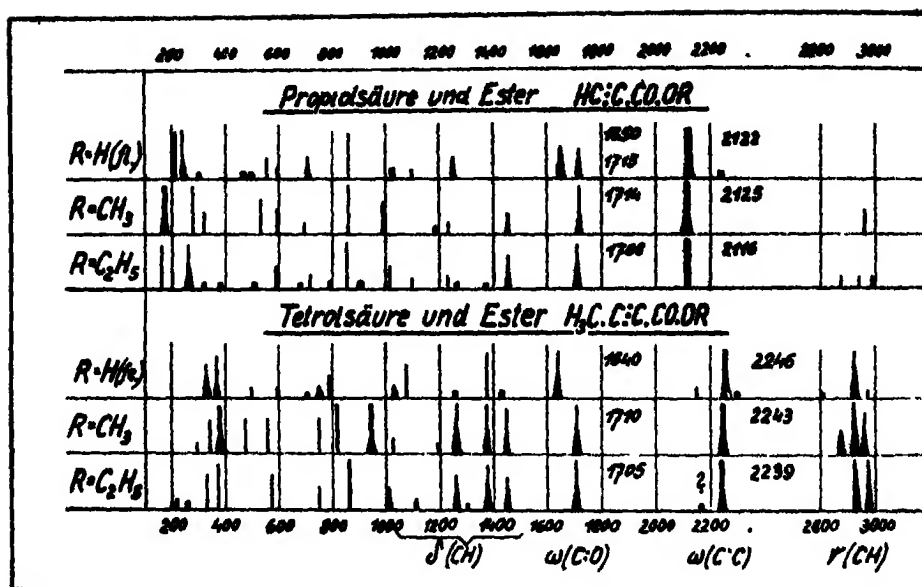


FIG 1

Die Ramanspektren der Propiol- und Tetrol-Säure und ihrer Ester. Die Spektren der ersteren sind noch zu ergänzen durch die in der Zeichnung nicht eingetragenen OH-Valenz-Frequenzen der Methin-Gruppe bei 3280

methylierten Benzolen) der an der Dreifachbindung sitzenden CH_2 -Gruppe zuordnen. Das Verständnis der Einzelheiten des übrigen Spektrums bereitet noch Schwierigkeiten, die vielleicht durch die Bearbeitung einiger weiterer homologer Säuren verringert werden können.

DIRECTIONAL VARIATIONS IN THE ABSORPTION AND THE FLUORESCENCE OF THE CHRYSENE MOLECULE.

BY K S KRISHNAN AND P K SESHAN

1 Single Crystals as Suitable Media for Studying the Directional Variations in Some of the Properties of Aromatic Molecules

COMPLETE X-ray analyses of the structures of several organic compounds, particularly of the aromatic class, have been made recently by Robertson (1933-38) and others. Since the molecules of these compounds retain their individuality in the crystal state, and their orientations in the crystals are known from the X-ray studies, the crystals are very suitable for the study of the directional variations of some of the properties of the molecules.

The directional variations in the magnetic and the optical polarisabilities of many of the aromatic molecules have been studied in this manner. Conversely, when the principal polarisabilities of the molecules are already known, the magnetic or the optical studies on the crystals can be utilized to obtain information regarding the orientations of the molecules in the crystals (Krishnan, 1929, Bhagavantam, 1929, Krishnan and Banerjee, 1933, 1935, Bernal and Crowfoot, 1935, Banerjee, 1938).

The absorption spectra of some of these crystals have been studied under polarised light (Krishnan and Seshan, 1934, Obreimov and Prikhodtjko, 1936), and it is found that for plane aromatic molecules much of the absorption is confined to light vibrating along directions in the plane of the benzene rings, vibrations along the normal to the plane being much less absorbed. Hence a study of the "pleochroism" of aromatic crystals can also be utilized for determining the molecular orientations in the crystals. Studying in this manner the polarisation of the absorption by single crystals of anthracene and chrysene, containing traces of naphthacene (2, 3-benzanthracene) as impurity, crystals of diphenyl containing fluorene as impurity, etc., one finds that the impurity molecules are oriented with their planes nearly parallel to those of the host molecules which accommodate them (Krishnan and Seshan, 1934).

The concentrations of the impurities can be controlled, and these crystals form therefore very convenient media for studying the fluorescence of the impurity molecules, and in particular the directional variations in their fluorescence, since the orientations of the impurity molecules in the crystals

are known approximately and we can excite the fluorescence by light vibrating along known directions with reference to the molecule, and can analyse the fluorescent radiations emitted along different directions for their polarisation. Some preliminary experiments on the fluorescence of naphthacene molecules, included as impurity in anthracene and chrysene crystals, showed that the excitation of fluorescence is due mostly to light-vibrations in the plane of the naphthacene molecule, vibrations along the normal to the plane exciting very little fluorescence. Similar results were also obtained from studies on the fluorescence of single crystals of 1, 2, 5, 6-dibenzanthracene, which could be obtained in very thin flakes.

In the present paper we report quantitative studies on the fluorescence and light-absorption of single crystals of pure chrysene. This substance was chosen because its crystal structure is known in detail from X-ray studies, and pure synthetic chrysene free from naphthacene and other fluorescent impurities could be easily obtained.

2 The Orientations of the Molecules in Chrysene Crystal

A quantitative X-ray analysis of the structure of this crystal has been made by Iball (1934). The crystal is monoclinic in the space group C_{2h}^6 (I 2/c) or C_2^2 (I c). Its unit cell has the dimensions

$$a = 8.34, b = 6.18, c = 25.0 \text{ A.U.}, \beta = 115^\circ 8'$$

and it contains 4 molecules of $C_{18}H_{12}$.

The molecule has a plane structure and it consists of four regular hexagons arranged as shown in Fig. 1. Let OA and OB be two directions in the plane of the molecule located as marked in the diagram.

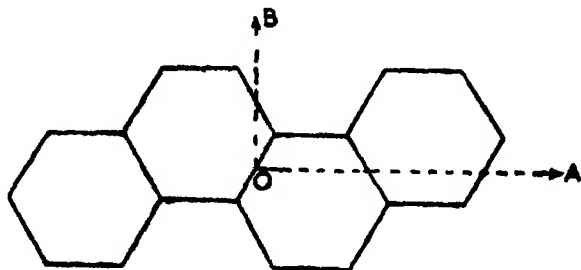


FIG. 1

Two of the molecules in the unit cell of the crystal are oriented in the same way, and their OA directions make with the a and the b crystallographic axes angles of $102^\circ 0'$ and $90^\circ 5'$ respectively, while their OB directions make

with the same axes angles of $118^{\circ} 4$ and $29^{\circ} 0$ respectively. The orientations of the other two molecules in the unit cell are obtained from the above orientations by reflection from the (010) plane.

The crystal as usually prepared is in the form of a flake parallel to the $c(001)$ plane. From the above angles defining the molecular orientations it is easily seen (1) that the molecular planes are nearly perpendicular to the plane of the flake, actually making with it an angle of 79° , (2) that their intersections with the plane of the flake make angles of $\pm 29\frac{1}{2}^{\circ}$ with the b -axis, and (3) that these intersections are very close to the OB axes of the molecules.

The orientations of the molecules in the crystal can also be deduced from measurements on its magnetic anisotropy, and are found to be practically the same as those obtained above from the X-ray analysis. Let δ be the angle which the molecular planes make with (001), and $+\phi$ and $-\phi$ the angles which the intersections of the molecular planes with (001) make with ' b '. Let χ_1 and χ_2 be the maximum and the minimum susceptibilities of the crystal in the (010) plane, and θ the angle which χ_2 axis makes with a . Also let K_{\parallel} be the susceptibility of the molecule along the normal to its plane and K_{\perp} that for directions in the plane. (The susceptibility will be practically the same along different directions in the molecular plane.) Then we can easily show that

$$\cos \delta = \sin \theta \sqrt{\frac{\chi_1 - \chi_2}{K_{\perp} - K_{\parallel}}},$$

$$\cos \phi = \cot \theta \cot \delta$$

Using these expressions, and the experimental values (Krishnan and Banerjee, 1935)

$$\theta = 13^{\circ} 1$$

$$\text{and } \chi_1 - \chi_2 = 170 \times 10^{-6}$$

$$K_{\perp} - K_{\parallel} = 218 \times 10^{-6}$$

per gram molecule, we obtain

$$\delta = 78\frac{1}{2}^{\circ} \text{ and } \phi = 28\frac{1}{2}^{\circ},$$

as compared with the X-ray values 79° and $29\frac{1}{2}^{\circ}$ respectively.

Since the molecular planes are nearly perpendicular to the plane of the crystal flake, and the OB axis of the molecule lies nearly in the plane, the directional variations in the absorption and the fluorescence of the molecule as we pass from the normal to the molecular plane to the OB axis in the plane can be easily followed.

3 Measurements on Fluorescence.

We shall first take up the study of the fluorescence. Chrysene has three diffuse fluorescence bands in the visible region, with their maxima at 4490, 4380 and 4200 Å respectively. Using a quartz mercury lamp as the source of light, and suitable light-filters for isolating some of the mercury lines, we found that the above fluorescence bands are excited strongly by the 3650 group of lines, and hardly, if at all, by the 4047 and the 4358 groups.

A thin flake of the crystal of about 1/20 mm thickness was used in our measurements. As we mentioned before, the plane of the flake is the (001) plane, and the two extinction lines in the plane will naturally be the a and the b axes. The general plan of the experiments was to excite the fluorescence by the radiations of the 3650 group incident normally on the crystal flake, either unpolarised, or polarised with the electric vector along the a or the b axis, and to study the fluorescence in the forward direction for its polarization and intensity. A sketch of the experimental arrangement used is given in Fig. 2. The light from a mercury lamp M is focussed, with the help of a lens L_1 , on a square aperture A having its sides vertical and horizontal respectively. Between L_1 and A are inserted a nicol N_1 to polarise the light suitably, and a Corning glass-filter F to isolate the 3650 group of radiations. C is the crystal flake mounted just behind the aperture and covering it completely, with its plane perpendicular to the path of the light, and its a or b axis vertical. The fluorescence in the forward direction, after passing

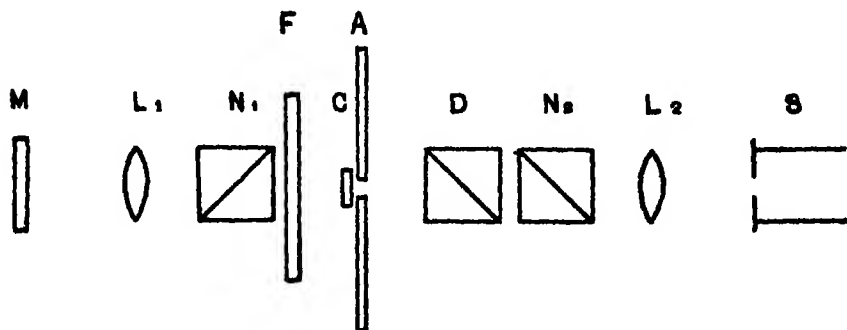


FIG. 2

through a double-image prism D , so oriented as to separate the images vertically, a nicol N_2 , and a lens L_2 , forms two images of the aperture A on the slit S of the spectrograph, one of them just above the other. The polarization of the fluorescence is determined by suitably rotating the nicol N_2 , so as to make the intensities of the two images of the fluorescence bands appearing in the spectrograms equal.

We shall mention here one simple result which enables us to dispense with the spectrograph, this is an advantage in view of the feeble intensity of the fluorescence. For any given excitation, *all the three fluorescence bands are found to be polarised to nearly the same extent*. Indeed as far as can be judged from the spectrograms every small region inside the bands also appears to have nearly the same polarization (except in the extreme violet, beyond about 4100 Å, where the two principal absorption coefficients in the plane of the crystal flake, which are unequal, begin to increase rapidly). This will be clear from Fig. 3, Plate XVI, which was taken with the principal plane of the analyser N_2 at 35° to the direction of the a axis of the crystal.

It would therefore be sufficient to compare the total intensities of the two polarised images of the fluorescent light formed at S, without analysing them spectroscopically, the photographic plate may be placed at S, and the images photographed directly. For this purpose, however, it would be necessary to cut off any of the incident radiations that may be transmitted by both the Corning glass-filter and the crystal. The filter transmits, in addition to the 3650 group of lines, some of the long wave-length lines also. Though the 1/20 mm thick crystal used in the experiment completely cuts off the 3650 group and the lines in its neighbourhood, some of the long wave-length lines transmitted by the filter are transmitted feebly by the crystal also. These were eliminated in our measurements by placing in the path of the fluorescent light a glass cell containing a dilute solution of sodium nitrite. The sodium nitrite filter served also to weaken considerably the tail of the fluorescence spectrum in the extreme violet, where, as we mentioned, owing to the rapid variations in the two principal absorption coefficients in the plane of the crystal, the apparent intensities of the two images are somewhat unequal.

4 Results

Measurements were made on the degree of polarization of the fluorescence in the forward direction, with the incident light-vibrations along with the a -axis of the crystal, and again with the vibrations along b . *For both the excitations* the a vibrations in the fluorescence were found to be less intense than the b vibrations, and the ratio of the intensities of the two vibrations was also the same for both, namely 0.49.

Now since the polarization of the forward fluorescence is the same whether the incident light-vibrations are along a or along b , we should naturally expect the same polarization with incident unpolarized light also. Removing the nicol N_1 in the experimental arrangement we measured again the polarization of fluorescence in the forward direction. The ratio of the intensities of the a and the b vibrations was the same as before, namely 0.49.

The value of 0.49 obtained in all the three measurements above for the ratio ρ of the intensities of the a to the b vibrations in the forward fluorescence requires correction on two accounts (1) The b vibrations in the fluorescence are absorbed more strongly by the crystal than the a vibrations. From a measurement of the absorption coefficients in the fluorescence region it was estimated that the b vibrations are weakened in relation to the a vibrations on this account in the ratio 0.85 : 1. Since the ratio changes slightly with wave-length, this estimate of its effective value should be regarded as only approximate. (2) The b vibrations of the fluorescent light lose by reflection at the back surface of the crystal about 4% more than the a vibrations. Making these two corrections we obtain for the true ratio of the intensities of the a to the b vibrations in the fluorescence the value $\rho = 0.40$.

5 The Significance of the Results

The result that the ratio ρ is independent of whether the incident light-vibrations are along the a axis or along b is very significant. It shows that in the (001) plane, to which we shall confine our attention at present, there are two unique directions, one on either side of the b axis, and making equal angles with it, such that it is only the resolved components of the incident electric vector along one or the other of these two directions, as the case may be, which can excite fluorescence in any given molecule. The electric vector of the fluorescent radiations from the molecule will also naturally be along the same direction. The ratio of the intensities of the a to the b vibrations in the fluorescence of the crystal as a whole, namely ρ , will then be determined only by the inclinations of the above directions to the a and the b axes. If $+\Phi$ and $-\Phi$ are the angles which these directions make with b , evidently

$$\rho = \tan^2 \Phi,$$

and one can readily understand why the ratio ρ should be independent of the direction of the incident electric vector in the (001) plane, and also why, over the whole region of fluorescence, ρ should have the same value. The absolute intensities of the a or the b vibrations, unlike their ratio ρ , will of course depend on the direction of the incident electric vector, and we shall postpone the consideration of their separate intensities to a later section, confining ourselves here to their ratio ρ .

The experimental value of ρ namely 0.40, corresponds to

$$\Phi = \tan^{-1} \sqrt{0.40} = 32^\circ,$$

i.e., the two unique directions mentioned above should lie on either side of the b -axis, making with it angles of 32° .

Now these two directions nearly coincide with the intersections of the molecular planes with the plane of the crystal flake (001), since the intersections make angles of $29\frac{1}{2}^\circ$ with b on either side. In other words, Φ is nearly the same as ϕ . We can conclude therefrom that among the various directions lying on the (001) plane, along which the electric vector may be incident, the excitation of fluorescence in any given molecule is a maximum when the electric vector is in the plane of the molecule, and it is practically nothing when it is along the projection of the normal to the molecular plane on (001). Considering the latter direction, along which the excitation of fluorescence is practically nothing, since there is no direction in the molecular plane which is closer to it than 79° , and since the normal to the molecular plane makes with it an angle of 11° only, we are forced to conclude that when the incident electric vector is along the normal to the plane of the molecule, there is hardly any fluorescence excited.

Our present experiments, beyond demonstrating that when the electric vector is incident along the OB direction in the plane of the molecule there is a strong excitation of fluorescence, do not enable us to draw any conclusions as to how the efficiency of excitation will vary with the change of direction of the electric vector in the plane of the molecule.

6 The Polarization of Fluorescence in State of Solution cannot give Information regarding the Anisotropy of Fluorescence of the Molecule

We should mention here that measurements on fluorescence in the liquid state or in state of solution in suitable solvents, even when the medium is made so highly viscous that molecular rotations are completely stopped, cannot give us any information regarding the anisotropy of fluorescence of the molecules. Suppose a parallel beam of plane polarised light with its electric vector along the z -axis traverses the solution in the x -direction, and that observations are made on the polarization of the fluorescence either in the forward direction (x), or in the transverse direction (y). Let us denote by r the ratio of the intensity of the weak component to that of the strong in the partially polarised fluorescent light. Let us suppose there is a unique direction in the molecule such that when the electric vector is incident along this direction there is maximum excitation of fluorescence, and that the fluorescent radiations so excited also vibrate along the same direction, and further that when the incident electric vector is along any direction perpendicular to the above unique direction in the molecule, there is no excitation of fluorescence at all. In other words, we assume that the fluorescence of the molecule would be that of a single linear oscillator fixed to the molecule. Assuming that the molecules in the medium have fixed random orientations,

the ratio r , as Perrin (1931) has shown, would be theoretically equal to $1/3$, corresponding to a 50 per cent polarization of the fluorescent light

If instead of the fluorescence being due to a single linear oscillator, it is regarded as due to more than one oscillator, along different directions fixed to the molecule, then because of the incoherence between the incident and the fluorescent radiations and the consequent incoherence in phase between the different oscillators in the same molecule, they will behave as though they were all independent of one another, and the resulting polarizations of fluorescence of the medium along the forward or the transverse direction would still only be 50 per cent, i.e., r would still be only $1/3$

If the medium is not sufficiently viscous and the molecules are free to rotate, then owing to the finite duration of the molecule in the excited state, the observed value of r would naturally be greater than $1/3$, we are not concerned with this aspect of the problem, which has been discussed in great detail by Perrin. What we wish to emphasise here is the result, which is not generally realised, that the polarization of the fluorescence of the solution, in which the molecules are oriented at random, is independent of the anisotropy of fluorescence of the molecule and cannot therefore give any information about the latter, and only measurements on a medium in which the molecules are regularly oriented, as in a crystal, can give such information. In this respect there is an essential difference between the phenomena of scattering and fluorescence

In this connection it is very significant that in all highly viscous solutions, whatever the fluorescing molecule may be, the ratio r does experimentally tend to approach a value close to $1/3$, i.e., the limiting value of the polarization for infinite viscosity is close to 50 per cent. (Perrin, 1931, Mitra, 1933, 1934)

7 *The Intensities of Fluorescence Excited Separately by the a and the b Vibrations (compared)*

Coming back to the observations on the chrysene crystal, if the explanation given in a previous section for the observed value of ρ , namely $\rho = \tan^2 \Phi = \tan^2 \phi$, is correct, then we should expect that for a *very thin crystal*, so thin that the absorption of the 3650 radiations which excite the fluorescence is negligible, the total intensity of forward fluorescence excited parallel to the a axis should be less than that excited by vibrations of the same intensity incident along the b axis, in the ratio $\tan^2 \Phi : 1$

It was not practicable, however, to verify this result directly, since even the thinnest crystal absorbs both the a and the b vibrations of 3650 very strongly, and to very different extents. In any actual crystal, owing to the

much stronger absorption of the b vibrations of the exciting light than of the a vibrations, the observed ratio R of the intensities of fluorescence excited separately by the two vibrations will naturally be greater than the theoretical value of $\tan^2 \Phi$ predicted for an ideally thin film. Actually with our 1/20 mm thick crystal, which absorbed both the a and the b vibrations of the incident 3650 radiations *completely*, the fluorescence excited by the a vibrations was found to be just stronger than that excited by the b vibrations, *i.e.*, for such a thick crystal, R is practically unity.

We can deduce from this observation one important result. Since both the a and the b vibrations of the exciting light are completely absorbed, and the b vibrations much more strongly than a , the penetration, or the effective thickness of the crystal producing the observed fluorescence, should be much greater when the incident vibrations are along a than when they are along b . To be more precise, the effective thickness for the two vibrations should be in the inverse ratio of the corresponding absorption coefficients. Since the observed ratio R is unity, instead of being equal to $\tan^2 \Phi$, as it would have been had the effective thicknesses been the same for both the vibrations, we should infer that the effective thickness for the a vibration is greater than that for b in the ratio $1/\tan^2 \Phi$, and since the effective thicknesses are inversely proportional to the absorption coefficients, that the absorption coefficient of the crystal for the 3650 region for the a vibrations should bear to the coefficient for the b vibrations the ratio $\tan^2 \Phi/1$.

Now since Φ is nearly equal to ϕ , the angle which the intersections of the molecular planes with (001) make with b , the obvious interpretation of the above result is this. We found that light-vibrations incident along the normal to the plane of the molecule do not excite its fluorescence and it is only vibrations in the plane that do. We are now forced to the conclusion that the molecular absorption also is practically nothing when the incident light-vibrations are along the normal to the plane of the molecule, and it is only vibrations in the plane that are absorbed by the molecule.

The close correspondence between the absorption spectra of the crystal for the a and the b vibrations is then easily understandable, since on the view presented here the effect of changing over from the a to the b vibrations, on the absorption, will be roughly equivalent to increasing the thickness of the crystal from $\tan^2 \phi$ to 1.

8 Direct Comparison of the Absorption Coefficients for the a and b Vibrations

Because of the very strong absorption of the 3650 group for both the vibrations, it was not possible to measure the absorption coefficients directly

and verify whether they bear the ratio $\tan^2 \phi = 1$. We have, however, made such measurements in the region of the first absorption band, which has a maximum, not very strong, at about 3970 Å U (see Fig 4, Plate XVI)

The light from an iron arc was rendered nearly parallel, and after passing through a large-sized nicol, was incident axially on the slit of a spectrograph. In front of the slit and close to it was mounted a screen with two small square apertures, one just below the other. One of them was covered completely by the crystal plate, with its a or b axis vertical. A rotating sector mounted just in front of the open aperture served to reduce the intensity of the light falling on it by a constant known amount, in the ratio 2.5 : 100 in our experiments. A further reduction in intensity which was necessary in order to equalize it in the 3970 region with the light transmitted through the crystal, was secured by shutting out the light through the open aperture after a certain fixed interval of time, while the exposure through the crystal was continued for a longer time, which was increased progressively in the different exposures. A few typical photographs near about the point of matching for the 3969 line of iron, which is the region of maximum of the first absorption band, is reproduced in Figs 5 and 6 (Plate XVI). In Fig 5 the incident light vibrations were along the a axis, and in Fig 6 along b .

The thickness of the crystal was measured by an optical method. The crystal flake was placed between two crossed nicols with its a and b axes at nearly 45° to the principal planes of the nicols, white light was allowed to traverse the system, and after transmission was analysed by a spectrograph. The refractive indices of the crystal for the a and the b vibrations, according to some unpublished measurements by Mr Sundararajan in this laboratory, are 1.615 and 1.787 respectively for the 5461 line, and 1.648 and 1.849 respectively for the 4358 line. The birefringence of the crystal plate is thus known for the two wave-lengths, and by counting the number of fringes which appear between these two lines in the above spectrogram—the number was actually 8.1—the thickness of the plate was calculated and was found to be 0.0055 cm.

Coming back to the absorption measurements, we shall give here only the final results. For the 3969 line, which, as we mentioned, is the region of maximum absorption in the first band, the ratio of the intensity of the transmitted light to that of the incident light (after correcting for the loss by reflections at the two surfaces) was 0.18 for the a vibrations, and 0.0037 for the b vibrations. Equating these ratios to $e^{-k_a t}$ and $e^{-k_b t}$ respectively, where t is the thickness of the crystal (0.0055 cm), and k_a and k_b are the absorption coefficients for the 3969 line for the a and the b vibrations respectively, we obtain

$$k_a = 310$$

$$k_b = 1020$$

approximately The ratio $k_a/k_b = 310/1020 = \tan^2 29^\circ$ The last angle is practically the X-ray angle ϕ which gives the inclination to the b -axis of the intersections of the molecular planes with (001) The value of Φ deduced in an earlier section from the fluorescence measurements was 32°

Thus the conclusion that the absorption coefficients of the crystal for the a and the b vibrations should bear approximately the ratio $\tan^2 \Phi : 1$ is verified experimentally, and hence also the obvious inference therefrom that light-vibrations incident along the normal to the molecular plane are not absorbed at all by the molecule

Since the vibrations which excite fluorescence strongly are also the vibrations which are absorbed strongly, and those which do not excite fluorescence are not absorbed at all, one is tempted to enquire whether after all the absorption by the molecule may not represent the energy expended in exciting fluorescence Such a simple connection between fluorescence and absorption however, offers difficulties, since some of the absorption bands are in regions whose wave-lengths are too long to excite fluorescence, and they are polarised just as strongly as the other absorptions We are continuing the studies on fluorescence with a view to elucidate the connection between the absorption and the fluorescence of these molecules

Summary

Chrysene crystal is monoclinic, and as usually prepared is in the form of a flake parallel to (001) The molecular planes are inclined at 79° to (001), and their intersections with (001) make angles of $+\phi$ and $-\phi$ with the b -axis, where $\phi = 29\frac{1}{2}^\circ$

The fluorescence of the crystal was excited by the 3650 group of lines of the mercury arc, incident normally on the flake, and was analysed in the forward direction for its polarizations and intensity The following results may be mentioned here

(1) Whether the incident vibrations are along a or along b , the a vibrations in forward fluorescence are much weaker than the b vibrations, the ratio of their intensities being 0.40, which is nearly equal to $\tan^2 \phi$ From this it is concluded that when the incident light-vibrations are along the normal to the plane of a molecule there is hardly any fluorescence excited in it, and that it is only vibrations in the plane that excite fluorescence

(2) With a crystal thick enough to absorb *completely* the exciting radiations, the intensities of forward fluorescence excited by the a and the b

vibrations separately, are practically equal. From this observation it follows that the absorption coefficients for the a and the b vibrations should bear the ratio $\tan^2 \phi = 1$. This conclusion is verified by direct measurements on the absorption coefficients.

The obvious interpretation of this result is that when the incident light-vibrations are along the normal to the molecular plane there is hardly any absorption, and it is only vibrations in the plane that are absorbed.

(3) The relation between fluorescence and absorption is discussed.

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b FIG 3
a



b FIG 4
a



FIG 5

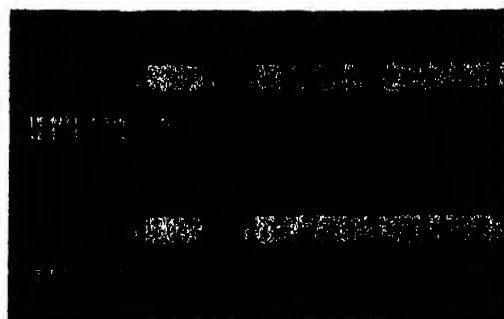


FIG 6

THE DIFFRACTION OF LIGHT BY SUPERSONIC WAVES.

BY N S NAGENDRA NATH *

(Trinity College, Cambridge)

1 Introduction

AN elementary theory of the diffraction of light by supersonic waves in liquids was put forward by Sir C V Raman and myself¹ to explain many of the important features of the phenomenon observed by Bar and others. The theory was developed under the restriction that a light beam undergoes no amplitude changes on its wavefront during its passage through the supersonic field. This restriction enabled us to get closed expressions for the intensities of the diffraction orders. Later, experimental conditions actually satisfying the above restriction were realised by Bar and Sanders who have reported reasonable agreement with our calculations. We have also developed the exact theory² without the above restriction. Though it explains certain of the features when the restriction is not satisfied experimentally, yet it is far from being satisfactory, as the expressions are too complicated. The exact theory developed by Extermann and Wannier³ suffers also from the same defect. They have only plotted the intensity diagrams of the diffraction orders for certain values of the parameters entering the theory. The purpose of this paper is to point out an extreme case where one can get closed expressions for the intensities of the diffraction orders. While the elementary theory is valid in the low frequency region (5 to 6 megacycles per second or less), the theory contained in this paper is valid in any frequency region so long as the supersonic field is not strong enough to excite the second and other higher orders. It is also found that in the very high frequency region, the first orders would be dominant over the higher ones.

Let us assume that the sound field creates a periodic fluctuation in the refractive index of the medium and consider the case when the direction of the incident light is normal to the direction of the sound waves. The amplitudes of the diffraction orders satisfy the equations²

$$2 \frac{d\Phi_r}{d\xi} - \Phi_{r-1} + \Phi_{r+1} = i\rho r^2 \Phi_r, \quad (1)$$

$$r = -\infty, \quad \dots, -1, 0, 1, \dots, \infty,$$

* Exhibition of 1851 Scholar.

where

$$i = \sqrt{-1},$$

$$\rho = \lambda^2 / \mu_0 \mu \lambda^{*2},$$

$$\xi = 2\pi\mu z / \lambda,$$

μ_0 = the refractive index of the medium,

μ = the amplitude of the fluctuation of the index,

λ = the wave-length of the incident light,

λ^* = the wave-length of the sound waves,

z = the width of the sound field along the direction of the incident light

The boundary conditions to be satisfied by Φ 's are

$$\Phi_0(0) = 1 \quad \text{and} \quad \Phi_r(0) = 0, \quad r \neq 0, \quad (2)$$

which mean that the intensity of the incident light is unity. If ρ is zero in (1), the solutions of (1) satisfying (2) are given by $\Phi_r(\xi) = J_r(\xi)$ where J_r is the Bessel function of the r th order. This corresponds to our elementary theory.

If ρ is very large, then the equation (1) can only be satisfied if

$$2 \frac{d\Phi_r}{d\xi} \approx ir\rho^2\Phi_r, \quad r \neq 0 \quad (3)$$

which means that

$$\Phi_r \approx A_r \exp(ir\rho^2\xi/2), \quad r \neq 0 \quad (4)$$

But A_r must nearly be zero by virtue of (2). If $r = 0$

$$\frac{d\Phi_0}{d\xi} \approx 0 \quad (5)$$

and hence $\Phi_0 = 1$ by virtue of (2). This means that when ρ is very large, the diffraction effect will not be prominent as is otherwise the case when ρ is nearly zero.

Let us assume that ρ is so large that the second and all other higher orders have vanishing amplitudes. In this case the equations are

$$\begin{aligned} \frac{d\Phi_0}{d\xi} + \Phi_1 &= 0, \\ 2 \frac{d\Phi_1}{d\xi} - \Phi_0 &= i\rho\Phi_1, \end{aligned} \quad (6)$$

as one can easily see that $\Phi_1 = -\Phi_{-1}$. If we put $\Phi_0 = A_0 \exp(i\lambda\xi)$ and $\Phi_1 = A_1 \exp(i\lambda\xi)$, it is easy to find out that λ satisfies the equation

$$2\lambda^2 - \lambda\rho - 1 = 0, \quad (7)$$

the roots of which are

$$\lambda_1, \lambda_2 = \frac{\rho \pm \sqrt{\rho^2 + 8}}{4}.$$

Thus the amplitudes can be written as

$$\begin{aligned}\Phi_0 &= A_0 \exp(i\lambda_1 \xi) + A_1 \exp(i\lambda_2 \xi) \\ \Phi_1 &= A_1 \exp(i\lambda_1 \xi) + B_1 \exp(i\lambda_2 \xi)\end{aligned}\quad (8)$$

By virtue of (2) and (6) we must have

$$\begin{aligned}A_0 + B_0 &= 1, \\ A_1 + B_1 &\approx 0, \\ A_1 + i A_0 \lambda_1 &= 0, \\ B_1 + i B_0 \lambda_2 &\approx 0\end{aligned}\quad (9)$$

Solving (9) we can write the solutions for Φ_0 and Φ_1 as

$$\begin{aligned}\Phi_0 &= \frac{1}{2} \left(1 - \frac{\rho}{\sqrt{\rho^2 + 8}} \right) \exp \left\{ i \left[\frac{\rho + \sqrt{\rho^2 + 8}}{4} \right] \xi \right\} \\ &\quad + \frac{1}{2} \left(1 + \frac{\rho}{\sqrt{\rho^2 + 8}} \right) \exp \left\{ i \left[\frac{\rho - \sqrt{\rho^2 + 8}}{4} \right] \xi \right\} \\ \Phi_1 &= \frac{i}{\sqrt{\rho^2 + 8}} \left[\exp \left\{ i \left[\frac{\rho + \sqrt{\rho^2 + 8}}{4} \right] \xi \right\} - \exp \left\{ i \left[\frac{\rho - \sqrt{\rho^2 + 8}}{4} \right] \xi \right\} \right]\end{aligned}\quad (10)$$

which may also be written as

$$\begin{aligned}\Phi_0 &= \left[1 - \frac{8}{\rho^2 + 8} \sin^2 \left\{ \frac{\sqrt{\rho^2 + 8}}{4} \xi \right\} \right]^{\frac{1}{2}} \times \\ &\quad \exp \left\{ i \left[\frac{\rho \xi}{4} - \tan^{-1} \left(\frac{\rho}{\sqrt{\rho^2 + 8}} \tan \left(\frac{\sqrt{\rho^2 + 8}}{4} \xi \right) \right) \right] \right\} \\ \Phi_1 &= \frac{2}{\sqrt{\rho^2 + 8}} \sin \left\{ \frac{\sqrt{\rho^2 + 8}}{4} \xi \right\} \exp \{ i \rho \xi / 4 \}\end{aligned}\quad (11)$$

It may be seen from (12) that the phase of the central order depends on the index fluctuation while that of the first order does not depend on it, as $\rho \xi$ is independent of μ . The intensities of the diffraction orders are given by

$$\begin{aligned}I_0 &= 1 - \frac{8}{\rho^2 + 8} \sin^2 \left\{ \frac{\sqrt{\rho^2 + 8}}{4} \xi \right\} \\ I_1 &= 1 - \frac{1}{\rho^2 + 8} \sin^2 \left\{ \frac{\sqrt{\rho^2 + 8}}{4} \xi \right\}\end{aligned}\quad (12)$$

If ρ becomes very large $I_0 \approx 1$ and $I_1 \approx 0$ in conformity with our earlier conclusion. If ρ is very small, $I_0 \approx 1 - \sin^2(\xi/\sqrt{2})$ and $I_1 \approx \frac{1}{2} \sin^2(\xi/\sqrt{2})$. As the second orders are not observed in this region only when ξ is small, the above expressions may be easily seen to be the approximations of $J_0^2(\xi)$ and $J_1^2(\xi)$.

Leaving these two extreme cases, it may be seen from (12) that when

$$\frac{\sqrt{\rho^2 + 8}}{4} \xi = \pi s$$

or
$$z = \frac{s}{\sqrt{\left(\frac{\lambda}{\mu_0 \lambda^2}\right)^2 + 8\left(\frac{\mu}{\lambda}\right)^2}}, \text{ where } s \text{ a positive integer, (13)}$$

the intensity of the first order is zero which means the absence of the diffraction effect

We have assumed here that ρ is so large that the second and other higher orders have vanishing intensity. We should thus expect reasonable agreement between (12) and one of the diagrams in Extermann and Wannier's paper³ in which the second order has a small intensity while all the higher orders are absent. This diagram corresponds to $\rho = 1$ and we should thus expect the validity of (13) when $\rho > 1$ (Extermann's θ and D are $\frac{1}{\rho}$ and $\rho \xi/2$ respectively in our notation). In the following diagram, the dotted

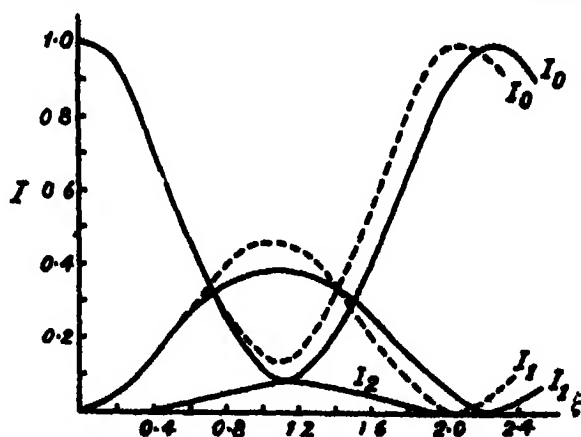


FIG. 1

The dotted curves practically coincide with the continuous ones of Extermann and Wannier for low values of ξ

curves are according to (12), while the continuous ones are taken from the paper of Extermann and Wannier. Complete agreement cannot be expected as our expressions (12) are valid only when the second and other higher orders are not present, which is not exactly the case as can be seen in the curve for the intensity of the second order which is not entirely negligible. If we remember that Extermann's curves were plotted from extensive

calculations, the usefulness of (12) when $\rho > 1$ may not be without significance, as he has only plotted three intensity diagrams two of which correspond to $\rho < 1$ and the remaining to $\rho = 1$

Before concluding we may point out the significance of (11) in the application of the theory to the diffraction of light by supersonic waves in solids. If we consider a longitudinal sound wave, it creates an index fluctuation given by an ellipsoid, two of whose axes lie in a plane perpendicular to the direction of the incident light and one of which lies along the direction of the sound wave. If the incident light is linearly polarised, we will have to decompose the incident light into two components, the polarisations of which lie along the above axes and consider the propagation of each independent of the other. It may be seen from (11) that the phases of the two components of the central order would be different as they depend on the principal index fluctuations which are different. Thus the resultant of the two components of the central order should be elliptically polarised. The first order would be linearly polarised as can be seen from (11), in the limits of the validity of the theory. In general, one should expect the diffraction orders to be elliptically polarised. But when $\rho \approx 0$, the phases of the diffraction orders do not depend on the index fluctuations and we should expect, as has been pointed out by Mueller and myself,⁴ that the diffraction orders would be linearly polarised.

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OERTLICHE EMPFINDLICHKEITS-UNTERSCHIEDE IN DER SCHICHTE DER PHOTOGRAPHISCHEN PLATTE.

VON O PAULSEN UND A W REITZ

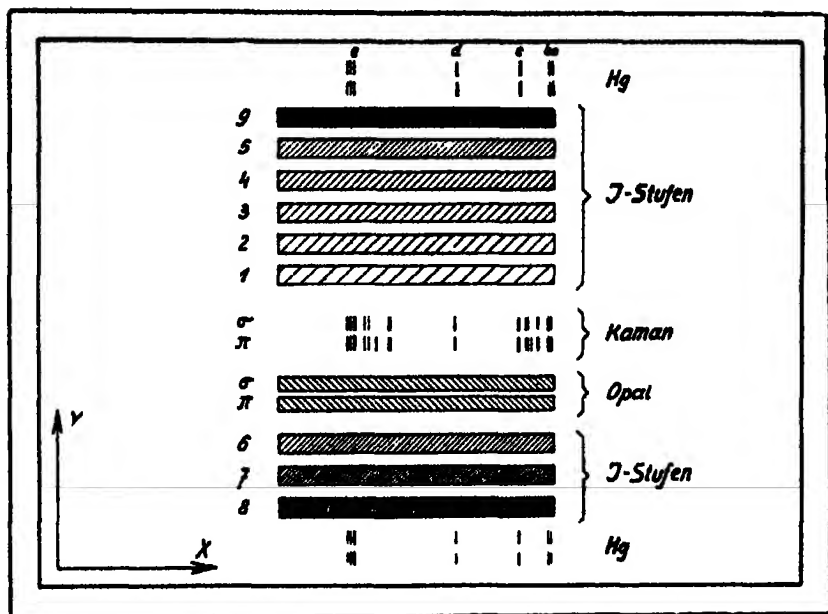
(182. Mitteilung aus dem Physikalischen Institut der Technischen Hochschule Graz)

(Mit 2 Figuren im Text)

Bei photographischen Intensitäts-Messungen benötigt man bekanntlich die Kenntnis der "Schwärzungs-" oder "Gradations-Kurve", die für die betreffende Plattensorte die Abhängigkeit der entwickelten Schwärzung von der aufgestrahlten Energiemenge darstellt. Man erhält sie, indem man mit Lichtintensitäten, deren Verhältnis bekannt sein muss, Intensitäts-"Stufen" oder "-Marken" auf die Platte druckt und deren Schwärzung mit dem Photometer misst. Die Schwärzungsmarken liegen naturgemäß auf verschiedenen Stellen der Platte, die Gradationskurve, auf der die zu untersuchenden Schwärzungen, die selbst wieder auf andern Stellen der Platte liegen, abgegriffen werden sollen, ist natürlich nur verwendbar, wenn die Empfindlichkeit der Emulsion an allen verwendeten Plattenstellen die gleiche ist. Man scheint in dieser Hinsicht keine systematischen Störungen zu befürchten und sich im allgemeinen damit zu begnügen, dem Plattenrand fern zu bleiben, es wäre ja auch schwierig, auf derselben Platte und auf denselben Stellen sowohl die Schwärzungskurve als auch lokale Empfindlichkeits-Unterschiede bestimmen zu wollen, insbesondere dann schwierig, wenn so wie beim spektrophotometrischen Arbeiten als dritte Unbekannte die Abhängigkeit der Gradationskurve von der Wellenlänge hinzukommt.

In dieser Lage ist man z. B. bei der Bestimmung der *Depolarisations-Verhältnisse im Streuspektrum*, wobei für die einzelnen durch ihre Frequenz definierten Raman-Linien das Intensitäts-Verhältnis der σ - und π -Komponente zu bestimmen ist. Bei diesen Versuchen liess uns ein günstiger Zufall erkennen, daß gewisse Störungen, die wir bis dahin als zufällige angesehen hatten, systematischer Natur und daher vermeidbar sind. Die im hiesigen Institut seit einigen Jahren verwendete "Polarisations-Apparatur" und ihre bis damals bekannten Fehlerquellen wurde von dem Einen von uns ausführlich beschrieben¹. Die Ungenauigkeit in der Messung des Depolarisations-faktors ρ_n wird durch Vermeidung des im folgenden besprochenen Plattenfehlers nicht unwesentlich verringert.

¹ A. W. Reitz, *Ztschr. physikal. chem.*, 1936, (B), 33, 368



FIGUR 1

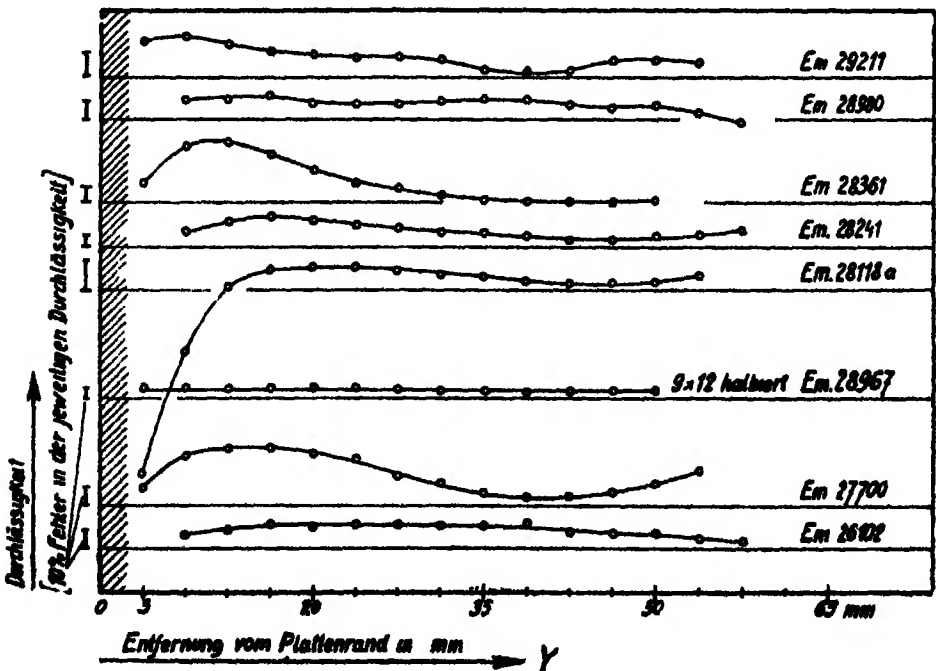
Die Ausnützung der Plattenfläche (6,5 mal 9 cm) für die zur Bestimmung der Polarisations-Verhältnisse im Raman-Spektrum nötigen Schwärzungen. Oben und Unten Streuspektrum der Hg-Lampe zur Festlegung des Zusammenhanges zwischen Platten-Ort und Wellenlänge. In der Mitte die π und σ -Komponente des Raman-Spektrums, darunter π und σ -Komponente eines mit einer Opallampe hergestellten kontinuierlichen Kontroll-Spektrums. Nr. 1 bis 9 Intensitäts-Stufen.

Bestimmt man nun zur Herstellung der Gradations-Kurve an irgend einer interessierenden Frequenzstelle (für einen bestimmten Wert λ) die Schwärzungen in den von 1 bis 9 in der Schwärzung zunehmenden Stufen, so ergab sich immer schon eine gewisse Streuung der Messdaten derart, daß insbesondere die Angaben für die Stufen 5, 6, 7, 8, 9, von denen laut Fig. 1 die mittleren drei in der unteren, die anderen in der oberen Plattenhälfte gedruckt worden waren, sich nicht in eine eindeutig glatte Kurve einfügen wollte. Wir benützten die Braunsiegel-Platte (Otto Perutz, München) und legen größte Sorgfalt auf genaueste Einhaltung der Versuchsbedingungen (Konstanz der Lichtquelle, Belichtungs- und Entwicklungs-Zeit, Rodinal-Entwickler 1:20, Pinsel-Entwicklung bei 18° C in volliger Dunkelheit, Konstanz der Photometer-Empfindlichkeit u. s. f.)

Als wir nun gelegentlich die Emulsion Nr. 28361 verwendeten, waren die Abweichungen in den Angaben der Stufen 6, 7, 8, so groß, daß sie nicht mehr als zufällig angesehen werden konnten und uns zwangen, der Sache

nachzugehen. Mehrfache Wiederholung des Stufendrucks auf verschiedenen Platten derselben Emulsion ergab *stets* ein Herausfallen dieser Stufenwerte, nur daß sie bei den einen Aufnahmen wesentlich zu tief, bei den andern wesentlich zu hoch lagen, und zwar trat das eine oder andere ein, je nachdem ob beim Einlegen der Platte jene Längskante, die den stärkeren Randschleier aufwies, unten oder oben zu liegen kam.

Daraufhin wurden verschiedene Emulsionen auf diesen Effekt hin geprüft, es wurde so wie in Figur 1 über die ganze Breite (y -Richtung) der Platte Stufen *gleicher* Intensität gedrückt, und an irgend einer Stelle x photometriert. Die so bestimmte Durchlassigkeit wurde als Funktion des Abstandes der Stufe von jener Längskante der Platte, die den stärkeren Randschleier (schraffiert in Fig. 2) aufwies, eingetragen. Ergebnis in Figur 2. Man ersieht aus ihr, daß diese systematischen örtlichen Empfindlichkeits-Unterschiede erstens recht beträchtliche sein und sich zweitens in manchen Fällen bis zur Plattenmitte erstrecken können.



FIGUR 2.

Systematische örtliche Empfindlichkeits-Unterschiede in der Schicht von Braunsegg-Platten.

Auch an anderen nicht von *Perutz* hergestellten Plattensorten wurden ähnliche Ergebnisse erhalten. Wir vermuten, daß es sich dabei, ebenso

wie beim Randschleier, um eine irgendwie in der Herstellung begründete, mehr oder weniger allgemeine Eigenschaft photographischer Platten handelt. Vielleicht ist sie schon in der Literatur beschrieben und wieder in Vergessenheit geraten. Jedenfalls hielten wir es für unsere Pflicht über diese Erscheinung zu berichten, da ihre Nichtbeachtung quantitative photographische Intensitäts-Messungen unter Umständen weitgehend entwerten kann.

Wir umgehen diese Schwierigkeit derzeit so, daß wir an Stelle von 9 mal 6, 5—Platten halbierte 9×12 —Platten verwenden derart, daß die durch Randschleier ausgezeichneten Kannten nun in die y -Richtung der Figur 1 zu liegen kommen. Dann findet man, wie Figur 2 zeigt (3. Kurve von unten), entlang dieser Richtung praktisch vollkommene Konstanz der Durchlässigkeit. Alle bisher auf solchen Platten in der Art von Figur 1 hergestellten Gradationskurven lassen sich *exakt* durch *alle* Messpunkte legen.

STUDIEN ZUM RAMAN-EFFEKT.

Mitteilung XCV: Stickstoffkörper XII. (Nitrogruppe.)

VON E. PENDL, A. W. REITZ UND R. SABATHY

(181. Mitteilung aus dem Physikalischen Institut der Technischen Hochschule Graz)

(Mit 2 Figuren im Text)

Die Schwierigkeiten bei der Deutung der Spektren der Mononitroparaffine, insbesondere das Auftreten einer Linienverdoppelung bei 1380 machen eine besondere Untersuchung notwendig. Die zur Erklärung dieser Verdoppelung vorhandenen Möglichkeiten, es handle sich um eine CH-Frequenz, um eine nicht zu NO_2 gehörige Kettenfrequenz, um Aufspaltung infolge *Fermi*-Resonanz werden Punkt für Punkt als mindestens höchst unwahrscheinlich nachgewiesen. Es bleibt offenbar nur die Annahme über, daß die Nitrogruppe zwei verschiedene Formen annehmen kann; doch erscheint es wünschenswert, diesen Schluss noch durch Beistellung weiteren Erfahrungsmaterials zu stützen.

A. Einleitung

BEIM Versuch, die Spektren der Nitroparaffine zu deuten, treten gewisse Schwierigkeiten auf, die im Falle der beiden niedrigsten Homologen-Nitromethan und -athan¹ ganz besonders ausgeprägt sind. Vor allem ist es die Unklarheit, die bezüglich der Bedeutung der Doppellinie bei 1380 cm^{-1} besteht, denn einer, der üblichen Formulierung entsprechend gebauten Nitrogruppe können *nur zwei* hohe Frequenzen zukommen. Für das Auftreten einer dritten Linie in diesem Frequenzbereich müssen andere Ursachen maßgebend sein: entweder handelt es sich um eine CH-Deformationsfrequenz oder es liegt ein Fall von Aufspaltung infolge *Fermi*-Resonanz vor. Man konnte vielleicht auch daran denken, den sog. "Tunnel-Effekt" zur Erklärung heranzuziehen, doch wollen wir hierauf zunächst nicht eingehen. Schließlich ist noch die Koexistenz zweier verschiedener Formen der NO_2 -Gruppe als Ursache der Linienverdoppelung bei 1380 denkbar.

Um über Lage und Verhalten der CH-Deformationsfrequenzen Auskunft zu erhalten haben wir Chlorpikrin, dessen Spektrum überhaupt keine CH-Frequenz enthalten kann, sowie (unter anderem) zwei sekundäre Nitroparaffine untersucht, bei denen die Methyl- bzw. Methylengruppe in α -Stellung durch eine Methynggruppe ersetzt ist. Leider scheiterte unsere Absicht an Nitro-tertiär-Butan zu spektroskopieren bisher an der Widerstandigkeit dieser Substanz.

Um über die Auswirkung einer *Fermi*-Resonanz entscheiden zu können, ziehen wir in Nitromethan und Chlorpikrin zwei möglichst verschiedenartige

¹ A. Dadiou, F. Jele, und K. W. F. Kohlrausch *SB Akad. Wiss. Wien*. 1931, 140, 293.

Moleküle zum Vergleich heran Um die experimentelle Grundlage für die Deutung ihrer Spektren zu erweitern, haben wir schließlich noch Polarisationsmessungen an diesen beiden Körpern durchgeführt

B Experimentelle Ergebnisse

(a) Die Ramanspektren

1 Nitromethan, CH_3NO_2 Zweimalige Destillation bei vermindertem Druck $K_{P_{120}} 49,4-50,4^\circ$, $K_{P_{700}} 101,3^\circ$ (Lit $K_{P_{700}} 102^\circ$) Pl 2717, m F, $t = 12$, Pl 2720, m F, enger Spalt, $t = 35$, Pl 2718, o F, $t = 8$, Pl 2719, o F, enger Spalt, $t = 36$ Ugd m, Sp st-sst, $n = 41$

TABELLE I

Nitromethan

	PH ²	GV ³	DK ⁴	M ⁵	PRS ⁶	Mittel
1	487 (3)	485 (2)	478 (3)	483 (m)	480 (8, b)	483 (8 b)
2				610 (s)	608 (3, b)	609 (3 b)
3	[711 (4)]	655 (3)	656 (4)	657 (mst)	656 (10 l)	656 (10 b)
4	917 (5)	916 (6)	917 (10)	918 (sst)	915 (12, b)	917 (12 b)
5	992 (1)					
6	1101 (1)	1111 (1)	1105 (1)	1109 (s)	1096 (3, b)	1104 (3 b)
7	1274 (1)					
8					1314 (2, b)	1314 (2 b)
9					1333 (2, b)	1333 (2 b)
10	1380 (5)		1373 (4)	1376 (sst)	1374 (7)	1376 (7)
11	1404 (5)	1396 (6)	1400 (7)	1402 (sst)	1403 (8)	1401 (8)
12	1564 (1)	1561 (1)	1563 (3)	1560 (m)	1554 (3 sb)	1551 (3 sb)
13					2766 (1, d)	2766 (1d)
14	2973 (4)	2961 (5)	2966 (8)	2968 (sst)	2965 (10 sb)	2967 (10 sb)
15		3042 (6)		3057 (s, sb)	3048 (3 sb)	3049 (3 sb)

² A Petrikaln, J. Hochberg, *ZS phys Chem*, 1929, (B) 3, 217 und 405

³ A S Ganesan, S Venkateswaran, *Ind Journ Phys*, 1929, 4, 196

⁴ A. Dadiou, K W F Kohlrusch, *S Ber Akad Wiss Wien* 1930, 139, 77

⁵ L. Médard, *Journ chim phys*, 1935, 32, 136

⁶ Pendl—Reitz—Sabathy, vorliegende Arbeit.

In Tab I ist das hier erhaltene Ergebnis den älteren Angaben der einzelnen Autoren gegenübergestellt. Dank der angewendeten, reichlichen Uebersetzung konnten wir die Existenz von drei neuen Linien-1314 (2b), 1333 (2b), 2766 (1d)-sicherstellen. Die von *Petríkalm-Hochberg* angegebenen Frequenzen 992 (1) Nr 5 und 1274 (1) Nr 7 sind offenbar nicht reell und bei $\Delta\nu = 711$ (4) Nr 3 dürfte wohl ein Rechenfehler vorliegen. Im übrigen besteht gute Uebereinstimmung zwischen den zusammengehörigen Werten. Die letzte Spalte enthält die aus jenen Angaben ermittelten wahrscheinlichsten Frequenzwerte, die Intensitätsangaben sind aus der vorletzten Spalte übernommen.

(2) *Nitro-1-propan*, $(\text{H}_3\text{C})_2\text{HC}\cdot\text{NO}_2$. Darstellung nach *V Mayer*⁷ durch Einwirkung von Isopropyl-jodid auf AgNO_3 . Starke Erwärmung und Entwicklung brauner Dämpfe. Eine Stunde Erwärmung auf dem Wasserbade, hierauf neuerliche Zugabe von AgNO_3 und Erwärmung. Zweimalige Destillation bei herrschendem, zweimalige bei vermindertem Druck Kp_{760} 59–60°, Kp_{724} 113–119° (Lit Kp_2 118°), $n_{\text{D}_1, 20} = 1,3950$ Pl 2949, m F, t = 14, bei Pl 2652, 0 F, t = 9 bildet sich ein weisslicher Niederschlag, gleichzeitig wird die Substanz tief gelb n = 38

$\Delta\nu = 275$ (2b) (e), 336 (1b) (e, c), 460 (1) (k, e, c), 522 (4) (k, e, c), 558 ($\frac{1}{2}$) (e), 631 (00) (e), 849 (5) (k, f, e, c), 900 (1) (e), 964 (00?) (e), 1100 (3) (k, e), 1140 ($\frac{1}{2}$) (k, e), 1278 (0) (k, e), 1305 (0) (k, e), 1355 (4) (k, e), 1398 (4) (k, e), 1450 (3 b) (k, e), 1552 (1) (k, e), 2922 (4) (k), 2945 (6) (k, e), (2992 (5 b) (k, e))

(3) *Nitro-sek-butan* $\text{H}_3\text{C}_2\text{HC}(\text{CH}_3)\cdot\text{NO}_2$. Herstellung analog den früheren Substanzen aus Sek Butyljodid und Silbernitrit unter Verwendung von Seesand. Einmalige Dest bei herrschendem Druck, zweimal bei vermindertem Druck Kp_{760} 56–58°, Kp_{700} 124–139° (Lit Kp cca 140°); $n_{\text{D}_1, 20} = 1,4028$. Die Substanz ist gelb und gibt starken Untergrund; Pl. 2664 und 2667, m F, t = 14, Ugd s st, Sp m, n = 21, nur Hge-Erregung, Ergebnis wenig befriedigend.

$\Delta\nu = 232$ (0), 288 ($\frac{1}{2}$), 360 ($\frac{1}{2}$), 408 (1), 520 (1), 843 (3), 965 ($\frac{1}{2}$), 1017 (1), 1115 (1), 1275 (4), 1354 (3), 1389 (3), 1455 (4b), 1554 (1), [1620 ($\frac{1}{2}$), 1673 ($\frac{1}{2}$)], 2872 (3), 2942 (4), 2981 (2)

(4) *Nitro-1-butan*⁸ $(\text{H}_3\text{C})_2\text{HC}\cdot\text{H}_2\text{C}\cdot\text{NO}_2$. Zu einer Mischung von AgNO_3 und reinstem Seesand wurde die äquimolare Menge Isobutyl-Jodid langsam

⁷ V Mayer. *Liebig's Ann. Chem*, 1874, 171, 39.

⁸ E Demole. *Liebig's Ann. Chem*, 1875, 175, 142.

zugetropft, eine halbe Stunde erwärmt und abdestilliert. Da noch unverändertes Jodid vorhanden war, wurde neuardings mit AgNO_3 behandelt. Das Destillat ist grün. Das Isobutylinitrit wurde durch fraktionierte Destillation entfernt, die Fraktion über 130° dreimal bei vermindertem Druck destilliert. $K_{p_{45}}$ $61-62^\circ$ (Lit K_p $137-140^\circ$), $n_{D, 20^\circ} = 1,4066$ Pl 2640, m F., t = 14, Pl 2641, o F., t = 9, schwache Gelbfärbung Ugd m, Sp st, n = 47

$\Delta\nu = 236 (\frac{1}{2}) (\pm e)$, $302 (\frac{1}{2}) (e)$, $325 (3) (\pm e)$, $374 (0) (e)$, $427 (3) (\pm e, c)$, $481 (2b) (\pm e, c)$, $563 (0) (e)$, $610 (2) (e)$, $624 (2) (e, c)$, $726 (0) (e)$, $826 (6) (k, e)$, $899 (5) (k, e)$, $960 (5) (k, e)$, $1021 (\frac{1}{2}) (k, e)$, $1133 (2) (k, e)$, $1176 (\frac{1}{2}) (e)$, $1232 (3) (k, e)$, $1283 (3) (k, e)$, $1345 (5b) (k, e)$, $1382 (9) (k, e)$, $1446 (6b) (k, e)$, $1549 (5) (e)$, $1629 (0) (e)$, $2874 (5) (k)$, $2907 (6) (k, e)$, $2938, (6) (k, e)$, $2972 (8) (k, e)$

(5) *Chlorpikrin*, Cl_3CNO_2 . Das Präparat von Kahlbaum wurde dreimal im Vakuum destilliert. $K_{p_{70}}$ $47,4-48,4^\circ$ $K_{p_{72}}$ $111,2^\circ$ (Lit $K_{p_{80}}$ 112°) Pl 2726, m F., t = 12, Pl 2727, o F., t = $5\frac{1}{2}$ Ugd s m, Sp st, n = 42

TABELLE II

Chlorpikrin

Milone ⁹	Médard ¹⁰	P R S ¹¹	Milone ⁹	Médard ¹⁰	P R S ¹¹
201 (2)	203 (ast)	200 (8)		900 (s, h)	901 ($\frac{1}{2}$)
	288 (st) }				1025 (00)
298 (2)	298 (st) }	292 (6b)			1105 (00)
	410 (s)			1310 (s)	1308 (6)
429 (2)	439 (ast)	438 (12b)	1337 (2)		
		519 (00 ??)		1349 (s)	1345 (3)
		673 (1)			1481 (00 ??)
720 (1)	706 (ast)	705 (7b)	1578 (2)		
848 (1)	842 (ast)	840 (8)		1607 (m)	1604 \pm 15 (5b)

Aus Tab II geht hervor, daß einige neue Linien festgestellt werden konnten, insbesondere $\Delta\nu = 673 (1)$. Dagegen geben unsere gut exponierten

⁹ M. Milone, *Gazz. chim. ital.*, 1933, **63**, 453

¹⁰ L. Médard, *Journ. chim., phys.*, 1935, **32**, 136.

¹¹ Pendl-Reitz-Sabathy, vorliegende Arbeit

Aufnahmen keinerlei Anhaltspunkte für die Existenz von $\Delta\nu = 410$ (Médard) und 1333, 1578 (Milone)

(b) Polarisationsmessungen

TABELLE III
Nitromethan, Polarisationsmessungen

		Mittelwerte		Einzelwerte					
				Pl 374		Pl 375		Pl 376	
$\Delta\nu$	I_s	ρ	I	ρ	I	ρ	I	ρ	I
480	8b	0,89	33	0,86	35	0,94	32	0,87	31
698	3b	dp	[12]	[0,86]	[13]	[0,92]	[12]	[1,17]	[12]
656	10b	0,40	64	0,38	64	0,41	64	0,41	64
915	12b	0,07	142	0,06	130			0,07	154
1096	3b	0,74	12	0,79	15	0,68	11	0,76	11
1314 1333	2b } 2b }	dp	[5]	(dp)	[(6)]	Unbrauchbar		[1,00]	[5]
1374	7	[0,33]	[40]	[0,34]	[85]			[0,30]	[97]
1403	8	[0,41]	[123]	[0,43]	[122]			[1,98]	[125]
1558	5ab	0,81	27	0,79	24			0,82	29
2766	1ab								
2905	10ab	0,09	85	0,12	82			0,06	88
3048 (Hg)	3a1	[0,96]	[28]	[0, 96]	[28]				

(1) In Tab III sind die Ergebnisse unserer Polarisationsmessungen an Nitromethan zusammengestellt. Aufnahme 374 wurde 18 Stunden exponiert, Nr 375 mit 36 Stunden mußte wiederholt werden, weil die Platte wegen eines Schichtfehlers im Bereich der höheren, von H_g erregten Ramanfrequenzen unbrauchbar war. $\Delta\nu = 656$ ist die Bezugslinie für die Reduktion der drei Aufnahmen auf gleiche, relative Intensitäten. Runde Klammern bei den Zahlenangaben bedeuten, daß dieselben wegen zu geringer Intensität der Linie unsicher sind, eckige Klammern weisen auf Fälschung durch Überdeckung oder durch sehr nahe liegende, starke Linien hin. Sicher depolarisiert sind $\Delta\nu = 480, 608$ (der auf die überdeckende Linie $\nu = 656$ entfallende Anteil ist in Tab III bereits in Abzug gebracht), die Doppel-
linie 1314, 1333, ferner 3048 und wahrscheinlich 1558 e-2766 konnte wegen zu geringer Intensität (Grünücke!) nicht ausgemessen werden.

(2) *Chlorpikrin*. Die Tab IV, über die Ergebnisse der Polarisationsmessungen enthält naturgemäß keine Angaben über die sehr schwachen Frequenzen 519, 673, 901, 1025, 1105, 1481 Depolarisiert dürfte nur die tiefste Frequenz $\Delta\nu = 200$ sein, den nachsthochsten Wert für ρ weist die NO_2 -Frequenz $\Delta\nu = 1604$ auf

$\Delta\nu = 438$ (12b) mit $\rho = 0,09$ gehört offenbar zur selben Schwingungsform wie $\Delta\nu = 915$ (12b) mit $\rho = 0,07$ in Nitromethan

TABELLE IV

Chlorpikrin, Polarisationsmessungen

		Mittelwert		Einzelwerte			
				Pl 377		Pl 378	
$\Delta\nu$	I_s	ρ	I	ρ	I	ρ	I
200	8	0,81	113	0,81	113	0,80	112
292	6b	0,66	158	0,70	159	0,62	157
438	12b	0,09	308	0,08	322	0,09	294
519	00**						
673	1						
705	7b	0,70	48	0,73	49	0,67	46
840	8	0,27	60	0,30	60	0,24	60
901	$\frac{1}{2}$						
1025	00						
1105	00						
1308	6	0,49	27	0,43	27	0,54	26
1345	3	[0,46]	[12]	[0,33]	[11]	[0,56]	[13]
1481	00**						
1604	5b	0,79	18	0,77	17	0,81	18

C Diskussion

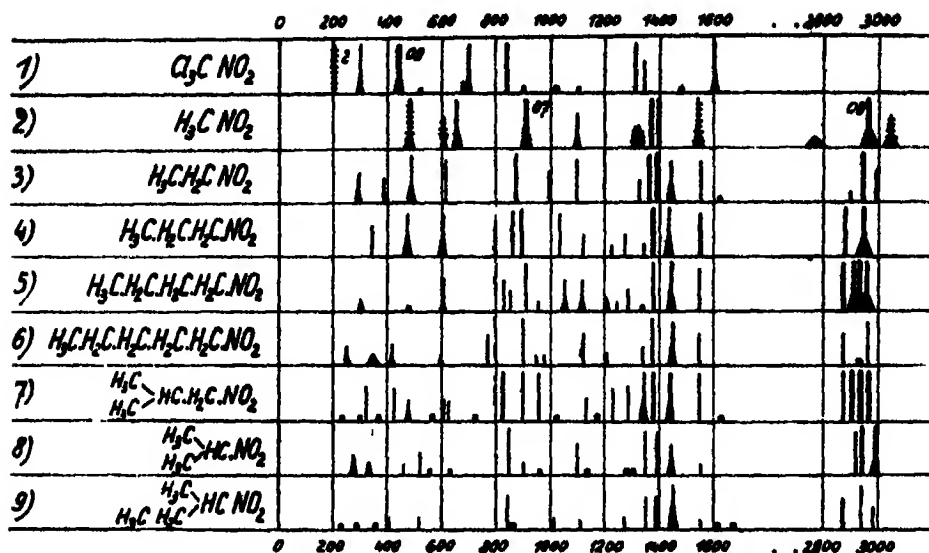


Fig 1

Die Ramanspektren von Chlorpikrin und den Mononitro-paraffinen

(a) *Frequenzwerte und Intensitäten* In Fig 1 sind unter Nr 2 bis 9 die Spektren der bisher bearbeiteten Mononitroparaffine zusammengestellt, als Nr 1 wurde überdies zu Vergleichszwecken das Spektrum von Chlorpikrin eingetragen. Die Zahlenwerte für die Zeilen 1, 2 und 7, 8, 9 entstammen dem vorhergehenden Abschnitt B, die Spektren der restlichen Zeilen 3 bis 6 sind aus der Arbeit von *Dadiou-Jele-Kohlrausch* (1c) übernommen. Eine neuerliche Durchsicht dieses Materials hat ergeben, daß auch in Nitro-n-butan eine zweite allerdings schwache Frequenz bei 1340 vorhanden ist. Als Ergänzung zur graphischen Uebersicht in Figur 1 seien im Folgenden die Eigenschaften (Frequenzwerte und relative Intensitäten) der drei zur Diskussion stehenden Linien auch zahlenmäßig zusammengestellt:

$\text{NO}_2 \cdot \text{CH}_3$	1376 (7)	1401 (3)	1551 (5)
$\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	1367 (7)	1394 (5)	1556 (4)
$\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	1346 (1)	1380 (8)	1553 (4)
$\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	1336 (0)	1382 (5)	1552 (4)
$\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	1342 (2)	1379 (5)	1551 (3)
$\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot (\text{CH}_2)_3$	1345 (5)	1382 (9)	1549 (5)
$\text{NO}_2 \cdot \text{CH} \cdot (\text{CH}_2)_3$	1355 (4)	1398 (4)	1552 (1)
$\text{NO}_2 \cdot \text{CH} \cdot (\text{CH}_2)_3 \cdot \text{C}_2\text{H}_5$	1354 (3)	1389 (3)	1554 (1)
$\text{NO}_2 \cdot \text{C}_2\text{H}_5$	1308 (6)	1345 (3)	1604 (5)

Strenge Lagenkonstanz kommt (abgesehen von Chlorpikrin) nur der höchsten Linie um 1550 zu, am wenigsten lagenkonstant ist die tiefste Frequenz mit einer Maximal-Verschiebung von 38 cm^{-1} , doch ist in dieser Hinsicht ein irgendwie charakteristischer Unterschied im Verhalten der beiden Linien um 1380 nicht festzustellen

In Bezug auf die *Intensitätsverhältnisse* jedoch sind Unterschiede im Verhalten dieser Linien bemerkbar. Obwohl die Eindeutigkeit der Aussage dadurch leidet, daß vom Äthylderivat angefangen die von Hgf und Hgg erregte CH-Deformations-Frequenz $\Delta\nu = 1450$ an die Stelle Hge—1395 und Hge—1345 zu liegen kommt und daher in manchen Fällen die Intensitäten fälscht, läßt sich doch feststellen, Die tiefere Frequenz weist starke Intensitäts-Schwankungen auf, die höhere nicht. Daraus läßt sich wohl mit einer gewissen Wahrscheinlichkeit folgern, daß die Intensitäten von $\Delta\nu = 1550$ und $\Delta\nu = 1390$ von andern Bedingungen abhängen, als die Intensität der tiefsten Frequenz. Das heisst mit andern Worten. Jehoren die beiden ersteren zur normalen NO_2 -Gruppe, dann gehört 1350 nicht dazu.

Endlich sieht man, daß dieses Linienpaar 1350 und 1390 weder in Chlorpikrin, daß doch überhaupt keine CH-Frequenzen besitzen kann, verschwindet, noch daß es merklich durch den Ersatz der Methylengruppe in α -Stellung durch Methin (Fig 1, 8 und 9) beeinflusst wird. Beides musste man erwarten, wenn es sich bei einer dieser beiden Linien um eine δ (CH)-Frequenz handelte. Auch dies scheint also nicht der Fall zu sein.

(b) *Deutung des Spektrums von Nitromethan*. Man hat noch zu fragen, ob nicht eine andere, nicht zur NO_2 -Gruppe gehorige, Ketten-Frequenz zur Erklärung einer dritten Linie im hohen Frequenzbereich herangezogen werden kann. Dazu ist eine überschlagsweise modellmäßige Berechnung mit plausiblen Annahmen über die Molekülkonstanten erforderlich. Vor Verwendung irgend eines Formelsystems ist jedoch zu klären, ob das Molekül die Methylgruppe als einheitliche Masse betrachtet als ebenes Gebilde behandelt werden darf. Eine diesbezügliche Entscheidung muß man aus dem Vergleich zwischen dem Ergebnis der Polarisations-Messungen und den Konsequenzen aus den Auswahlregeln abzuleiten versuchen.

Die Kette von Nitromethan ist ein Viermassensystem mit 3 Valenz- und 3-Deformationsfrequenzen. Ebenheit vorausgesetzt, kommt ihm die Symmetrie C_{2v} zu, falls mit der Figurenebene, die z -Achse mit der C-N-Bindung zusammen. Die hierfür geltenden Auswahlregeln¹³ sind in Tabelle V wiedergegeben. ω_3 und ω_4 gehören zu Deformations-Schwingungen in der

¹³ K. W. F. Kohlrausch, *S.R.E. Ergänzungsband*, S. 44.

Modellebene, ω_s zu einer Deformation *senkrecht* zu σ_x , die Schwingungsformen sind in Fig 2 schematisch dargestellt Ist das Molekül aber uneben, dann fällt die bisherige Figurenebene σ_x als Symmetrieelement fort und die vorher nur im Bezug auf σ_x unterschiedenen Schwingungstypen gehören nun

- TABELLE V
Nitromethan, Auswahlregeln

Typ	$\sigma_x \sigma_y$	Auswahlregeln	eben, C_{2v}	nicht eben, C_s
A_1	s s	p M_z	3 $\omega_1 \omega_2 \omega_3$	$\rightarrow 4 \omega_1 \omega_2 \omega_3 \omega_s$
A_2	as as	dp ia	0	
B_1	as s	dp M_x	1 ω_s	
B_2	s as	dp M_y	2 $\omega_4 \omega_5$	$\rightarrow 2 \omega_4 \omega_5$

ein und derselben Rasse an (Uebergang in Tab 5) ω_s ist demnach im ebenen Molekül als depolarisiert, im pyramidenförmigen als polarisiert ($\rho < 6/7$) zu erwarten Da im Spektrum an $H_3C \cdot NO_2$ auf Grund von Intensität und Polarisationszustand $\Delta \nu = 915$ sicher als "Pulsationsfrequenz" identifiziert werden kann und da die inneren Frequenzen der Methylgruppe nicht unter 800 cm^{-1} liegen, sind unter dieser Frequenz-Grenze außer ω_s nur noch die beiden Deformationsfrequenzen ω_3 (s) und ω_4 (as) zu erwarten, deren Polarisationszustand von der erwähnten Symmetrieharabsetzung unberührt bleibt Es sind also im Falle einer ebenen Kettenkonfiguration unter 800 cm^{-1} eine polarisierte und zwei depolarisierte Linien zu erwarten, andernfalls umgekehrt zwei polarisierte und eine depolarisierte Das Experiment entscheidet zugunsten der Symmetrie C_{2v} (480, dp, 608 dp, 656 p)

Hat man sonach hinreichend Grund anzunehmen, daß die Kette mindestens nicht stark von der Ebenheit abweicht, dann kann man mit den bekannten Formeln rechnen, die für ein ebenes, verzweigtes, axialsymmetrisches Viermassen-Valenzkraftsystem¹³ gelten Es ist bei solchen Ueberlegungen stets aufschlussreicher den Uebergang zwischen zwei Spektren als diese selbst mit den aus der Modelltheorie abgeleiteten Ergebnissen zu vergleichen In unserm Falle haben wir den Anschluss an das wohlbekannte Aceton¹⁴ gewählt Für die Modellkonstanten (bezüglich Bezeichnung siehe Fig 2) wurde gesetzt "Aceton" $m_1 = m_2 = 16$, $M = 14$, $s_1 = 1,15$, $s_2 = 1,35$, $f_1 = 10 \cdot 10^5 \text{ dyn-cm}$, $f_2 = 4 \cdot 10^5$, $d_1 = 0,4 \cdot 10^5$, $d_2 = 0$, $7 \cdot 10^5$;

¹³ K. W. F. Kohlrausch, *S.R.E. Ergänzungsband*, S. 68, Nr. 12.

¹⁴ K. W. F. Kohlrausch, *ebenda*, S. 141.

$2\alpha = 120^\circ$ "Nitromethan" $m_1 = m_2 = 16$, $M = 14$, $s_1 = 1,35$, $s_2 = 1,15$, $f_1 = 4 \cdot 10^8$, $f_2 = 10 \cdot 10^8$, $d_1 = 1,0 \cdot 10^8$, $d_2 = 0,7 \cdot 10^8$, $2\alpha = 120^\circ$ Der Vergleich zwischen dem Ergebnis dieser stark schematisierenden Rechnung und den Molekülspektren, bezw dem Uebergang zwischen denselben ist in Fig 2 durchgeführt Im Molekülspektrum von Aceton wurden der Uebersichtlichkeit halber die CH-Frequenzen weggelassen

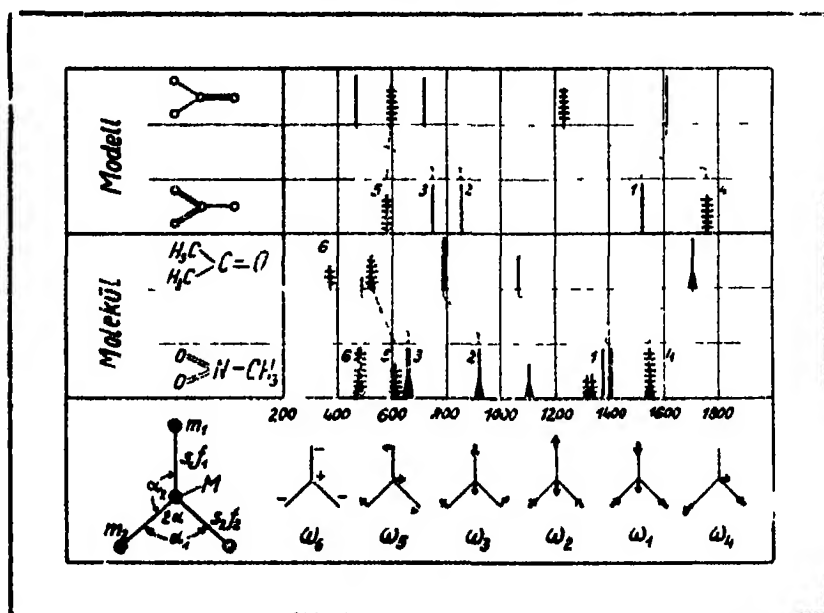


FIG 2

Der Uebergang Aceton \rightarrow Nitromethan

Die qualitative Uebereinstimmung zwischen Rechnung und Experiment ist so gut, daß sich eindeutig folgern läßt. Setzt man die übliche dieser Diskussion zugrundegelegte Konfiguration der Nitrogruppe voraus, dann ist in dem fraglichen Bereich (über 1300) die Existenz einer *dritten Kettenfrequenz ausgeschlossen*. Diese Aussage läßt sich ohneweiteres auf den Fall des Chlorpikrins übertragen, das ebenfalls nach der üblichen Formulierung seiner Struktur nur zwei hohe Frequenzen aufweisen dürfte.

(c) *Fermi-Resonanz?* Im Spektrum des Chlorpikrins findet sich eine Linie, deren Frequenz die Bedingung für das Eintreten der Fermi-Resonanz, $2\omega_x \approx 1330$, erfüllen würde, es ist die schwach polarisierte Linie ($\rho = 0,70$) bei 700. Damit die Resonanz zur Wirkung gelange, wird man allerdings vielleicht noch die weitere Bedingung stellen dürfen, daß es sich bei dieser Frequenz um die zur Nitrogruppe gehörige Deformationsschwingung handelt,

denn Schwingungen, die zu weit voneinander entfernten Gruppen im Molekül gehören, durften einander kaum hinreichend aufschaukeln können. Es sei dahingestellt, ob diese Bedingung hier erfüllt ist. Jedenfalls ist bei Nitromethan schon die erstere Voraussetzung nicht erfüllt; die einzige, dort in Frage kommende Linie liegt bei 656 ($\rho = 0,40$), ihre Oktav 1312 stimmt recht wenig mit dem Schwerpunkt 1388 des Dubletts überein. Wir glauben daher, daß auch ein solcher Erklärungsversuch für die Verdoppelung *nicht in Betracht kommt*.

(d) *Schlussbemerkung* Somit scheint ein Ausweg zur Beantwortung des eingangs aufgeworfenen Problems nur in der Annahme gegeben zu sein, daß die *Nitrogruppe zwei verschiedene Formen annehmen kann*. Ehe wir jedoch auf diese Möglichkeit ernsthaft eingehen und daraus Folgerungen ableiten, mochten wir doch noch weiteres Versuchsmaterial beibringen. Womöglich sollen Beobachtungen an Nitro-tertiär-Butan ergänzende Aussagen über die Rolle der CH-Frequenzen bringen, Neumessungen an dem bisher nur unvollständig bekannten Spektrum des Brompikrins können Beiträge zur Frage nach dem Einfluss von *Fermi*-Resonanz bestellen. Und endlich wären Untersuchungen an den ähnlich gebauten Ionen der Essig- und Trichloressigsäure u. a. m. heranzuziehen.

RAMAN EFFECT AND CHEMICAL CONSTITUTION.

Influence of Constitutive and Other Factors on the Double Bonds in Organic Compounds.

Part I—Coumarin.

BY G V L N MURTI AND T R SESHADRI.

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THE large amount of existing data on the Raman spectra of organic substances indicate considerable variations in the $C=O$ and $C=C$ frequencies depending upon the location of the groups in compounds which are differently constituted. These seem to correspond in a general way to the well-known differences in the chemical behaviour of these groups in different situations. Whereas chemical reactions are capable of indicating only larger differences, the physical method using Raman spectra seems to be capable of indicating even small changes in the nature of these groups. It is therefore proposed to examine in detail the $C=O$ and $C=C$ frequencies of suitable organic compounds of various types.

With the above end in view the Raman spectra of coumarin and dimethyl- γ -pyrone in carbon tetrachloride solution were studied by us more than a year ago. Meanwhile Venkateswaran¹ published a note in *Current Science* recording the Raman spectrum of coumarin in the solid state and in the molten condition. Though there was a general agreement between our results obtained with the solution and his relating to the solid, there were certain noteworthy differences particularly in regard to the carbonyl frequency. With a view to clarify the position we have now examined the Raman spectrum of coumarin in the solid state and in solution in various solvents and present the important features of the results in this paper.

As the exciting radiation Venkateswaran employed the 4046 Å U and 4077 Å U lines, the 4358 Å U of the mercury are being almost completely cut off by means of a filter of iodine in carbon tetrachloride. Since the Raman lines characteristic of the ethylenic and carbonyl double bonds fall within the region 1500 to 1800 cm^{-1} , we were interested in that part of the spectrum and therefore employed the 4358 Å U line as the more suitable one using a filter of a saturated solution of sodium nitrite. However, in order to check the results, pictures have been taken without using any filter and lines occurring within the region 1000 to 1800 cm^{-1} noted. The solvents were rendered dust-free by repeated slow distillation and a pure sample of

coumarin was used for the experiments. The same slit width was employed in all cases so as to facilitate comparison of the diffuse lines.

The Raman lines obtained by us and those recorded by Venkateswaran in the region 1000 to 1800 cm^{-1} are given in the following table. The numbers within brackets indicate visual estimates of the intensities.

*TABLE I

Coumarin in CCl_4	Coumarin in CHCl_3	Coumarin Solid (Authors)	Coumarin Solid (Venkateswaran)
1030 (1)	1030 (3)	1030 (1)	1031 (7)
1102 (3)	1096 (3)	1100 (3)	1098 (6)
1125 (3)	1123 (3)	1128 (3)	1120 (7)
1158 (3)	1156 (3)	1156 (3)	1152 (6)
1178 (10)	1181 (10)	1181 (10)	1173 (8)
1228 (4)	1229 (4)	1228 (4)	1228 (6)
1257 (2)	1262 (4)	1260 (4)	1259 (4)
1330 (4)	1332 (8)	1328 (6)	1324 (8 b)
			1361 (6)
			1396 (3)
			1415 (3)
1457 (2)	1460 (1)	1457 (2)	1451 (7)
1492 (2)	1493 (4)	1486 (4)	1483 (7)
1570 (8)	1569 (8)	1567 (8)	1562 (10)
1610 (6)	1609 (6)	1604 (6)	1610 (6)
1625 (6)	1631 (6)	1620 (6)	1623 (6)
		1708 (6)	1709 (8)
	1720 (6 b)	1731 (6)	1729 (8)
1742 (6)		.	..

*The lines corresponding to the solvents have appeared unaltered in the solutions.

It will be noticed that there is a fair general agreement between the four sets of results. The following points are however noteworthy —

(1) In our pictures the lines $1361, 1396, 1415 \text{ cm}^{-1}$ that were observed by Venkateswaran were absent. They were definitely absent when 4358 Å U excitation was employed. On the other hand when 4046 Å U line was used it was difficult to observe Raman lines 1361 and 1415 cm^{-1} because in the same places the fairly powerful lines 1178 and 1228 cm^{-1} excited by 4077 Å U fall

(2) Of the three lines $1570, 1610$ and 1625 the first two could be attributed to the $\text{C}=\text{C}$ linkage in the benzene ring and the last to the ethylene linkage present in the pyrone ring, since benzene gives the Raman shifts 1585 and 1606 and ethylene the shift 1620 . Though the pyrone double bond is situated in a ring it is highly reactive for addition reactions like ethylene and hence its resemblance to ethylene in the Raman frequency is justifiable.

(3) The Raman frequency attributable to the carbonyl group is highly interesting. In carbon tetrachloride solution it is 1742 cm^{-1} , in chloroform it comes down to 1720 and is rather diffuse whereas in the solid it is clearly resolved into a doublet equally spaced on either side of 1720 . The $\text{C}=\text{O}$ frequencies of a few closely allied compounds are given below —

Methyl cinnamate	. 1712	Benzylidene acetone	1666
Ethyl cinnamate	1706	Benzylidene acetophenone	1668
Coumarin	. 1742	Dimethyl- γ -pyrone	. 1678†

The $\text{C}=\text{O}$ in coumarin which is a typical example of an α -pyrone differs markedly from that present in dimethyl- γ -pyrone. The former belongs to the ester or lactone type chemically and the latter to the ketones. The grouping of the γ -pyrone along with the unsaturated ketones is therefore quite acceptable. Coumarin exhibits a rather high $\text{C}=\text{O}$ frequency as compared with the unsaturated esters. This increased strength of the $\text{C}=\text{O}$ bond is probably due to its existence in the ring which exhibits a far greater stability than ordinary esters and lactones. For this comparison we have taken the frequency of the $\text{C}=\text{O}$ of coumarin obtained in CCl_4 solution since as explained below we consider that in this solution the coumarin molecule exists in the normal state.

In order to get more data with a view to explain the variation in Raman frequencies of the double bonds of coumarin, the Raman spectra of the compound in benzene, carbondisulphide, acetone and methyl alcohol have also

† Our unpublished work.

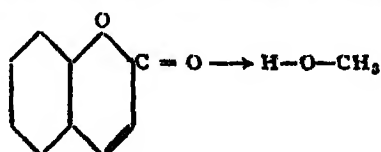
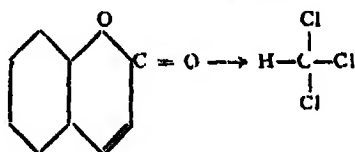
been studied The C = O and C = C frequencies obtained with the solution using the different solvents and in the solid state are given below :—

TABLE II.

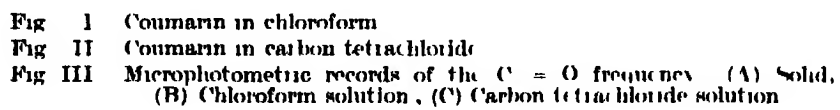
Coumarin in	C = O	O = O
CCl ₄	1570, 1610, 1625	1742
C ₆ H ₆	1569, 1610, 1624	1736
CS ₂	1568, 1610, 1626	1740
CH ₃ CO CH ₃	1568, 1611, 1625	1738
CHCl ₃ *	1569, 1609, 1621	1720
CH ₃ OH	1571, 1609, 1624	1721
Solid	1567, 1604, 1620	1708, 1731

* Coumarin is more soluble in chloroform than in any of the solvents employed and hence the Raman spectrum in this solvent was studied at three different concentrations. It was found that the concentration has no effect on the frequencies of the Raman lines

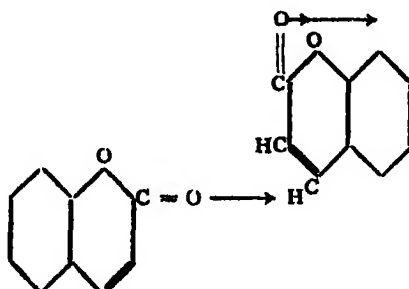
It will be noticed that the ethylenic C = C frequencies are practically unaffected in the different states whereas the C = O frequency is considerably influenced The first four agree amongst themselves and differ from the second group of readings The results obtained with the non-polar solvents like CCl₄, C₆H₆, and CS₂, may be taken as representing the normal state of the molecule practically unaffected by neighbouring molecules of coumarin or of the solvent The lowering of the frequencies in polar solvents like CHCl₃, and methyl alcohol seems to be due to the weakening of the C = O bond by combination with the solvent molecules as represented below through the



formation of a co-ordinate bond Though acetone is a polar solvent it is similar in behaviour to carbon tetrachloride, etc, since it cannot affect the C = O bond in coumarin. It was noted in this case that the C = O frequencies of the solvent and of the solute were quite independent of each other and quite definite.



The splitting of the $C=O$ frequency in the spectrum of the solid is rather difficult to explain. A similar splitting was observed by Bonino² in the case of hydroxymethylene camphor and he suggested that it may be due to the existence of resonance in the molecule. Though resonance exists in the coumarin molecule also as shown by Govinda Rao,³ the above explanation cannot hold good in the present case of coumarin since in the solutions in non-polar solvents where resonance is not prohibited the phenomenon is absent. Obviously this splitting is not due to the free molecule itself but arises as due to intermolecular effects. If we take the average of the two split components the single line for the solid should be in 1720 cm.^{-1} and this is the $C=O$ frequency given by the solutions in polar solvents. The lowering of the frequency and diffused nature or splitting seem to occur together. In the solid state the $C=O$ bond may be weakened by the mechanism given below.



All chemical reactions indicate that the position 4 in the pyrone ring has a positive charge thus indicating deficiency of electrons and the possible point of attack for the $C=O$ bond of the neighbouring molecule.

Summary

The Raman spectrum of coumarin in the solid state and when dissolved in various solvents has been examined with reference to (1) the $C=C$ and (2) the $C=O$ frequencies. Of the three frequencies belonging to (1) which are fairly constant throughout, the two lower ones represent the aromatic double bonds of the benzene ring and the third represents the ethylene double bond of the pyrone ring. The $C=O$ frequency is considerably low in the solid state as well as in the solutions with certain polar solvents. This is attributed to the weakening of the $C=O$ bond by the formation of hydrogen bonds through co-ordination.

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ON AN INEQUALITY CONCERNING LATTICE SUMS.

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AND

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§ 1 Introduction.

THE present investigation arose out of an attempt to examine the suggestion put forward by Raman and Krishnan¹ that the optical anisotropy of the molecules of a liquid tends to diminish when the influence of the neighbouring molecular field is taken into consideration. We started with the model of a rhombic lattice of static dipoles, but it was soon found that this model was inadequate for the purpose on hand. There arose, however, in the course of the investigations some inequalities connected with lattice sums which presented many points of mathematical interest. Specially in view of the fact that, although the actual evaluation of lattice sums figures prominently in the literature, the question of inequalities of such sums has nowhere been treated, we have thought it desirable to have them placed on record here.

§ 2 Statement of the inequality

Consider a rhombic lattice with the constants a, b, c , and let the origin be chosen at any one molecule situated at a corner of the lattice. The co-ordinates of any other molecule can be taken as $(n_1 a, n_2 b, n_3 c)$ where n_1, n_2, n_3 are integers. The potential due to a doublet at r is given by

$$\left(p, \text{grad } \frac{1}{r} \right) = \frac{x p_x}{r^3} + \frac{y p_y}{r^3} + \frac{z p_z}{r^3},$$

where p is the moment of the dipole. Hence the components of the force due to this potential are given by

$$F_x = - \frac{\partial \phi}{\partial x} = \frac{1}{r^5} \left\{ p_x (3x^2 - r^2) + 3xy p_y + 3zx p_z \right\}$$

and the total force

$$\begin{aligned} E_x &= \sum F_x = \sum \frac{1}{r^5} \left\{ p_x (2n_1^2 a^2 - n_2^2 b^2 - n_3^2 c^2) + 3n_1 n_2 ab p_y + 3n_1 n_3 ca p_z \right\} \\ &= \sum \left\{ p_x (2n_1^2 a^2 - n_2^2 b^2 - n_3^2 c^2) + 3n_1 n_2 ab p_y + 3n_1 n_3 ca p_z \right\} \\ &\quad (a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{\frac{5}{2}} \\ &= S_{11} p_x + S_{12} p_y + S_{13} p_z \end{aligned}$$

From considerations of symmetry $S_{12} = S_{13} = 0$. It might also be noticed that for a cubic lattice ($a = b = c$) we also have $S_{11} = 0$. In an exactly similar manner we can introduce the sums S_{22} and S_{33} . The difference

$$S_{11} - S_{22} = 3 \sum_{n_1, n_2, n_3} \frac{(a^2 n_1^2 - b^2 n_2^2)}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{\frac{r}{2}}}$$

The problem with which we are concerned in this paper is to find out whether this difference is positive or negative when $a > b$. For this purpose we consider the more general series

$$f(a, b, c) = \sum \frac{a^\lambda n_1^2}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^r} \quad (1)$$

examine its convergence, and then the inequalities $f(a, b, c) \gtrless f(b, a, c)$ in the case of three and two dimensions (i.e., a plane lattice). The results are given in the following two sections

§ 3 Proof in the case of a rhombic lattice

The summation in (1) can be assumed to be taken over all positive and negative values of n_1, n_2, n_3 excluding $n_1 = n_2 = n_3 = 0$. The terms of the series are less than the corresponding terms of the series

$$\sum \frac{a^{\lambda-2}}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{r-1}}$$

Comparing this with

$$\sum \frac{1}{(n_1^2 + n_2^2 + n_3^2)^{r-1}}$$

we see that the original series converges for $r > 5/2$. Let $a/b = \mu > 1$. Then we prove the following results

$$f(a, b, c) > f(b, a, c) \quad \text{if } \lambda \geq 2r \quad (2)$$

$$f(a, b, c) < f(b, a, c) \quad \text{if } \lambda \leq 2r - 3 \quad (3)$$

The method of proof adopted is the well-known process of transformation of series due to Kronecker. Now

$$\frac{\lfloor r \rfloor}{a^r} = \int_0^\infty e^{-at} t^{r-1} dt, \quad a > 0$$

Take $a = \pi (a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)$. Then we obtain

$$\int_0^\infty e^{-\pi (a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2) t} t^{r-1} dt = \frac{\lfloor r \rfloor}{\pi^r} \cdot \frac{1}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^r}$$

Hence,

$$f(a, b, c) = \frac{a^\lambda \pi^r}{\Gamma(r)} \int_0^\infty \sum n_1^2 e^{-\pi(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)t} \cdot t^{r-1} dt, \quad (4)$$

the validity of the operation effected above being too well known to be repeated here. Now let,

$$\omega(x) = \sum_{-\infty}^{\infty} e^{-\pi^2 x^2}, \text{ then}$$

$$\omega'(x) = -\pi \sum n^2 e^{-\pi^2 x^2}.$$

We can write (4) in the form,

$$\begin{aligned} f(a, b, c) &= \frac{a^\lambda \pi^{r-1}}{\Gamma(r)} \int_0^\infty \sum \pi n_1^2 e^{-\pi a^2 n_1^2 t} \sum e^{-\pi b^2 n_2^2 t} \sum e^{-\pi c^2 n_3^2 t} \cdot t^{r-1} dt \\ &= -\frac{a^\lambda \pi^{r-1}}{\Gamma(r)} \int_0^\infty \omega(b^2 t) \omega'(a^2 t) \omega(c^2 t) t^{r-1} dt \end{aligned}$$

Taking $a^2 t = v$, we get

$$f(a, b, c) = -\frac{\pi^{r-1} a^{\lambda-2r}}{\Gamma(r)} \int_0^\infty \omega\left(\frac{b^2 v}{a^2}\right) \omega\left(\frac{c^2 v}{a^2}\right) \omega'(v) v^{r-1} dv \quad (5)$$

In an exactly similar manner we obtain,

$$f(b, a, c) = -\frac{\pi^{r-1} b^{\lambda-2r}}{\Gamma(r)} \int_0^\infty \omega\left(\frac{a^2 v}{b^2}\right) \omega\left(\frac{c^2 v}{b^2}\right) \omega'(v) v^{r-1} dv \quad (6)$$

$$f(a, b, c) - f(b, a, c) = A$$

$$\int_0^\infty \omega'(v) v^{r-1} \left\{ \omega(\mu^2 v) \omega\left(\frac{c^2 v}{b^2}\right) - \mu^{\lambda-2r} \omega\left(\frac{v}{\mu^2}\right) \omega\left(\frac{c^2 v}{a^2}\right) \right\} dv \quad (7)$$

where $\mu = \frac{a}{b} > 1$, and A is a positive constant

Now we show that the integrand in (7) is positive for $\lambda > 2r$, and negative for $\lambda < 2r - 3$, for all values of v . Since $\mu > 1$

$$\mu^2 v > \frac{v}{\mu^2} \quad \text{and} \quad \frac{c^2 v}{b^2} > \frac{c^2 v}{a^2}$$

From the fact that $\omega(x)$ is a decreasing function it follows that

$$\omega(\mu^2 v) \omega\left(\frac{c^2 v}{b^2}\right) < \omega\left(\frac{v}{\mu^2}\right) \omega\left(\frac{c^2 v}{a^2}\right)$$

Hence, if $\lambda > 2r$,

$$\omega(\mu^2 v) \omega\left(\frac{c^2 v}{b^2}\right) < \mu^{\lambda-2r} \omega\left(\frac{v}{\mu^2}\right) \omega\left(\frac{c^2 v}{a^2}\right).$$

Further, we observe that $\omega'(v)$ is throughout negative and hence the integrand is throughout positive. This proves (2)

To prove (3), we apply the functional equation of $\omega(x)$, viz.,

$$\omega(x) = \frac{1}{\sqrt{x}} \omega\left(\frac{1}{x}\right)$$

from which we have,

$$\begin{aligned} \omega(\mu^2 v) &= \frac{1}{\mu \sqrt{v}} \omega\left(\frac{1}{\mu^2 v}\right), \quad \omega\left(\frac{c^2 v}{b^2}\right) = \frac{b}{c \sqrt{v}} \omega\left(\frac{b^2}{c^2 v}\right), \\ \omega\left(\frac{v}{\mu^2}\right) &= \frac{\mu}{\sqrt{v}} \omega\left(\frac{\mu^2}{v}\right), \quad \omega\left(\frac{c^2 v}{a^2}\right) = \frac{a}{c \sqrt{v}} \omega\left(\frac{a^2}{c^2 v}\right) \end{aligned}$$

Hence the expression inside the brackets in the integrand of (7) is equal to

$$\begin{aligned} &\frac{b}{c\mu v} \omega\left(\frac{1}{\mu^2 v}\right) \omega\left(\frac{b^2}{c^2 v}\right) - \frac{a\mu^{\lambda-2r+1}}{c v} \omega\left(\frac{\mu^2}{v}\right) \omega\left(\frac{a^2}{c^2 v}\right) \\ &= \frac{b}{c\mu v} \left\{ \omega\left(\frac{1}{\mu^2 v}\right) \omega\left(\frac{b^2}{c^2 v}\right) - \mu^{\lambda-2r+3} \omega\left(\frac{\mu^2}{v}\right) \omega\left(\frac{a^2}{c^2 v}\right) \right\} \end{aligned} \quad (8)$$

Now

$$\frac{1}{\mu^2 v} < \frac{\mu^2}{v}, \quad \frac{b^2}{c^2 v} < \frac{a^2}{c^2 v}, \quad \text{therefore}$$

$$\omega\left(\frac{1}{\mu^2 v}\right) > \omega\left(\frac{\mu^2}{v}\right), \quad \text{and} \quad \omega\left(\frac{b^2}{c^2 v}\right) < \omega\left(\frac{a^2}{c^2 v}\right)$$

Hence, if $\lambda < 2r - 3$, it follows that the expression inside the brackets in (8) is positive. Hence in this case the integrand in (7) is throughout negative, and this proves (3). In particular we obtain, for $\epsilon > 0$, the inequalities

$$\sum \frac{a^{2+2\epsilon} n_1^2}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{\frac{3}{2} + \epsilon}} > \sum \frac{b^{2+2\epsilon} n_2^2}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{\frac{3}{2} + \epsilon}}, \quad (9)$$

and,

$$\sum \frac{a^2 n_1^2}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{\frac{3}{2} + \epsilon}} < \sum \frac{b^2 n_2^2}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{\frac{3}{2} + \epsilon}} \quad (10)$$

which answers the question raised in § 2

§ 4 The case of the plane lattice

In this case we put $c = 0$, and take $r > 3/2$ for the convergence of the series that arises. The discussion for (2) is the same as before. The corresponding expression obtained in this case is

$$f(a, b) - f(b, a) = A \int_0^\infty \omega'(x) x^{r-1} \left\{ \omega(\mu^2 x) - \mu^{\lambda-2r} \omega\left(\frac{x}{\mu^2}\right) \right\} dx. \quad (11)$$

where A is some positive constant. Now, we have

$$\omega(\mu^2 x) = \frac{1}{\mu \sqrt{x}} \omega\left(\frac{1}{\mu^2 x}\right), \text{ and } \omega\left(\frac{x}{\mu^2}\right) = \frac{\mu}{\sqrt{x}} \omega\left(\frac{\mu^2}{x}\right),$$

and the expression within the brackets in (11) can be written as

$$\frac{1}{\mu \sqrt{x}} \left\{ \omega\left(\frac{1}{\mu^2 x}\right) - \mu^{\lambda-2r+2} \omega\left(\frac{\mu^2}{x}\right) \right\}$$

Since

$$\frac{1}{\mu^2 x} < \frac{\mu^2}{x}, \quad \omega\left(\frac{1}{\mu^2 x}\right) > \omega\left(\frac{\mu^2}{x}\right)$$

Hence, if $\lambda < 2r - 2$ we obtain that this is throughout positive, i.e., the integrand is throughout negative. Thus the inequality (3), $f(a, b) < f(b, a)$ is valid even when $\lambda < 2r - 2$, unlike the case of three dimensions. In particular we may notice the following inequalities

$$\sum \frac{a^{2-\epsilon} n_1^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}}} < \sum \frac{b^{2-\epsilon} n_2^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}}} \quad (\epsilon > 0) \quad (12)$$

where, if $\epsilon = 1$, we get (2)

$$\sum \frac{a^2 n_1^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}}} < \sum \frac{b^2 n_2^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}}} \quad (12')$$

i.e., $S_{11} < S_{22}$ if $a > b$. Also

$$\sum \frac{a^{1+2\rho-\epsilon} n_1^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}+\rho}} < \sum \frac{b^{1+2\rho-\epsilon} n_2^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}+\rho}} \quad (13)$$

$$\sum \frac{a^{3+2\rho+\epsilon} n_1^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}+\rho}} > \sum \frac{b^{3+2\rho+\epsilon} n_2^2}{(a^2 n_1^2 + b^2 n_2^2)^{\frac{3}{2}+\rho}} \quad (14)$$

We might observe, in conclusion, that the method adopted in the previous section can be applied to the very general series

$$f(a, b, c, \dots, k) = \sum \frac{a^\lambda n_1^2}{(a^2 n_1^2 + b^2 n_2^2 + \dots + k^2 n_k^2)^r},$$

and leads to the results that while (2) is valid, the inequality (3) is valid for $\lambda < 2r - k$. However, when $2r > \lambda > 2r - k$, the method we have adopted does not yield any definite result.

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RAMAN SPECTRA OF TERPENES.

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THE period during which Raman effect has been available as a tool for the elucidation of molecular structure has been one in which much useful data have been accumulated. So much so, it is now impossible for authors of monographs or of bibliographies on the subject to include comprehensive and co-ordinating tables of data and deal with them critically. Consequently the exact position with respect to the usefulness of Raman spectral methods as applied to certain types of chemical substances is frequently uncertain. One group of substances for which a large volume of scattered data has been recorded is the terpenes and, arising from conversations with Professor J. L. Simonsen, the author has endeavoured to collect all the existing results* and submits them in this paper. The purpose of the paper is to present in tabulated form, the experimental results of workers in this field, to compare the results of different investigators for the same substance, to correlate data on substances considered chemically to be structurally related, to co-ordinate and examine critically the assertions made by certain authors regarding the constancy of the Raman frequency of certain groups, to consider whether the claims which have been made in the literature regarding the application of Raman spectral methods to the identification of terpenes and to the analysis of terpene mixtures are spectroscopically justifiable, and to give a complete bibliography.

Before proceeding to an examination of the data contained in the tables, it is well to draw attention to some important facts. For a complete study of any molecule it is necessary to know its Raman and infra-red spectra. The more complicated the molecule, the more complex will both spectra be and, accordingly, it will become increasingly difficult to work out the normal modes of vibration and to ascertain their spectroscopic activity. Every molecule, irrespective of its molecular complexity, should have $3n - 6$ (n = number of atoms in the molecule) normal modes of vibration. Whether these are active in both Raman and infra-red spectra, or in one only, or are forbidden in both will depend on an application of spectroscopic selection

* The bibliographies provided by Kohlrausch⁴⁵ and by Hibben⁴² have been of most valuable assistance in this connexion.

rules and on the symmetry of the molecule. For a full discussion of molecular structure a knowledge of the state of polarisation of the Raman lines and of their intensities (*not* visually estimated) is necessary. Moreover, it must be borne in mind that spectroscopic selection rules, valid for the gaseous state, appear to break down when applied to the liquid state.¹ Consequently frequencies forbidden in one spectrum (Raman or infra-red) may appear faintly for the liquid state, although absent in the gaseous state.

In many of the papers under review inadequate description of experimental technique is given. The duration of exposure, an important factor, is frequently omitted. Excitation by unfiltered radiation from a mercury arc is always suspect because of the appearance of faint lines of mercury which may mask Raman lines or which, as sometimes happens, are mistaken for Raman lines. Important as these considerations are, there is a still more important fact particularly, but not peculiarly, applicable to terpenes. It is almost, if not absolutely, impossible to be certain that the substance is perfectly pure. For many terpene groups it is well known that members are never completely separable, but that each member is always more or less contaminated with its isomerides.† This fact seems to have been overlooked by many of the workers whose results are under consideration. Yet the significance of it should be apparent. Since this difficulty of obtaining pure material for examination does exist, it is quite impossible, for many substances, to draw conclusions regarding their structure from their Raman spectra.

Experimental Values

The data are contained in Tables I–VIII, the intensities are given (in parenthesis) in the nomenclature of the paper from which the data are taken since it is obviously impossible to transform the various units employed into a uniform scheme.

Before discussing these data critically and comprehensively attention will be drawn to any particular features of interest in the tables.

For comparative purposes the results for isoprene are included in Table I.

Table II is interesting principally for the comparison of the data for limonene, the agreement between the seven sets of results is good but not complete. The two sets of results given by Dupont and his collaborators^{22, 23} differ in one important connection, *viz*, the numerical value of the

† For instance, too little attention would appear to have been paid to the well-known "tautomerism" of the many members of the terpenes series containing the isopropenyl-isopropylidene group.

frequencies between 1600 and 1700 cm^{-1} . As will be shown later the precision with which these frequencies can be determined is of paramount importance in detecting the constituents of a mixture. Such variations in the same region are shown also in the data for α -phellandrene and Δ^1 -*p*-menthene.

In Table III, which contains the data for monocyclic terpenic alcohols and esters, there is one point which calls for special comment. An examination of Bonichon's results⁴ for α -terpineol, isopulegol, menthol, and their esters reveals the surprising fact that the majority of the lines of the alcohol appear in the identical position in the esters and with unchanged intensities. It is extremely doubtful if such close agreement is indeed experimentally realisable, and certainly it is not so in the experience of the present author. Furthermore, the contention submitted here is fully substantiated by examining the experimental values recorded for bornyl and isobornyl esters (Table VIII) and for myrtanol and isomyrtanol and their esters (Table VII), although there is great similarity, there is not complete identity.

Some of the data in Table IV is subject to criticism similar to that given in the last paragraph. Comparison of the data of Bonichon⁴ with those of Dulou¹⁰ shows complete agreement in the numerical values of practically every displacement for which these authors each report spectra. At first sight this would appear to arise from the reproduction in one paper of data communicated originally in the other. However, this does not seem to be the explanation since the two sets of intensities are often considerably different (*cf.* carvone and carvomenthone) and displacements marked "assez nette" in one paper are "raies floues" in the other. The more usual type of agreement expected in Raman effect is exemplified, for instance, by comparison of the results of Bonino and Cella⁶ for menthone with those of Dulou.¹⁰

The derivatives of thujane all give spectra very rich in lines (Table V). The spectrum of sabinene has been determined by three independent workers and their results are in very satisfactory agreement. That recorded by Matsuno and Han¹¹ shows two displacements of 2964 and 2966 cm^{-1} having visually estimated intensities of (6) and (4*bd*) respectively. These cannot be experimental values because even with a spectrograph of very high resolving power, it would be extremely difficult to separate two strong lines so close together. Moreover the fact that one of the pair is broad and diffuse is a further argument in disproving their authenticity. The comment is made because of a great tendency in much work on terpenes to claim an unattainable accuracy of measurement.

The derivatives of carane in Table VI call for no special comment except to mention here that data for two fractions, said to consist

predominantly of Δ^3 -carene, are reproduced from the paper of Dupont and Joffre²⁷

On examining the data in Table VII it is found that by comparing the results obtained for α -pinene by Dupont, Daure and Allard²⁷ with those of Dupont and Joffre²⁷ a very puzzling point emerges. Without a single exception, the values recorded by the latter authors are *exactly* 5 cm^{-1} lower than those in the other paper, even the broad band between 1400 and 1500 cm^{-1} is shifted *en bloc* across the spectrum by 5 cm^{-1} . The intensities of the lines are usually identical. Results for β -pinene are also contained in the same references and present the same extraordinary shifting of almost the entire spectrum by 5 cm^{-1} . It is difficult to believe that such results were obtained either fortuitously or experimentally.

Table VIII calls for no special comment.

Discussion

The comments embodied in the preceding section generally indicate an unfortunate tendency, not confined by any means to the study of terpenes, for authors to extend the attainable accuracy and reproducibility of results to a quite impossible degree. There are also in the tables certain results (*e.g.*, limonene⁶⁰) given to 0.1 cm^{-1} . Unquestionably, with a spectrograph of high resolving power, such accuracy would be obtainable for an *intense, sharp* line but the determination of faint or diffuse lines to this accuracy is, to say the least, a moot point. And, moreover, such high accuracy is not demanded by the nature of the investigations being reviewed.

It would be impossible to deal in detail with the many points which emerge from an examination of the results on terpenes. Accordingly only the salient features will be considered.

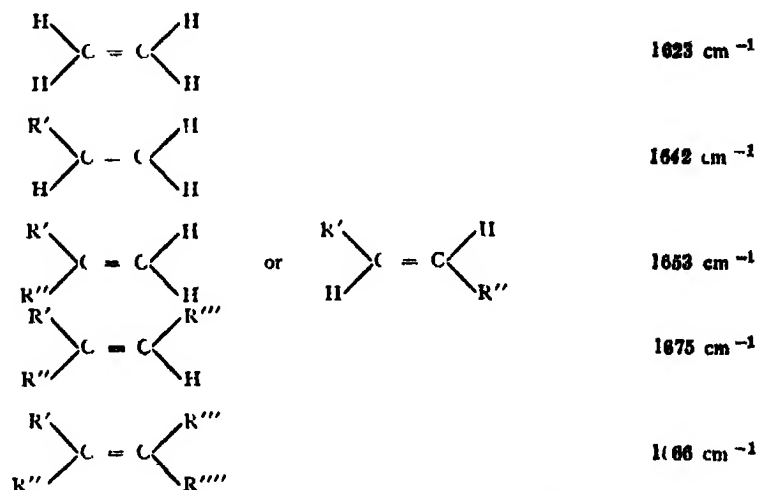
(a) *Comparison of different sets of data on the same substance*—For most substances listed in the tables there exist no confirmatory results and it is thus better to await such confirmation before accepting existing data unreservedly. Where data can be compared, agreement between the different sets is, on the whole, satisfactory. Certain sets of data are obviously incomplete and are therefore unsatisfactory for comparison purposes. For the others, apparently complete, there are often discrepancies in the intensities assigned by different authors to corresponding displacements. This may or may not be serious because the assignment of the intensity of an individual line in a complicated spectrum by visual estimation is more a question of physiology and psychology than of physics. Some of the recorded intensities must be accepted as very arbitrary. When the strongest line is

assigned a numerical intensity value of, say 15, it is difficult to appreciate what is meant by the intensity of a diffuse line to which the value 1 has been assigned. Also it is difficult to attach any value to fine intensity distinctions of (say) 4 and 5. Such criticism might be considered pedantic and academic, and the author would subscribe wholeheartedly to this view were it not for the fact that, as will be shown later, the arbitrarily assigned intensity values have been applied to problems dealing with the detection of the constituents of a terpene mixture.

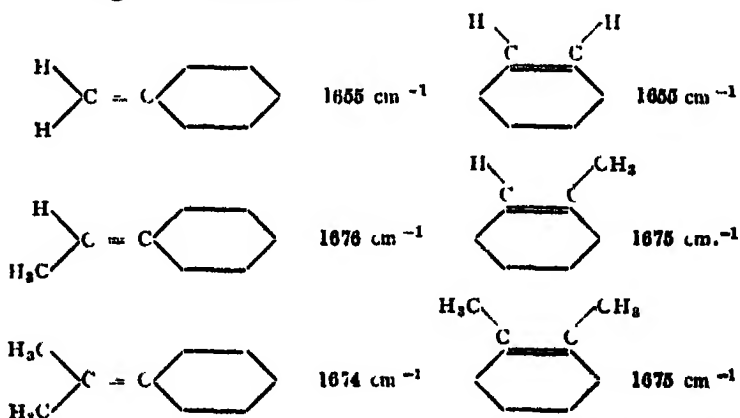
(b) *The spectra of optically active substances*—The identity of the spectra of the *dextro* and *laevo* forms of a substance has been amply demonstrated by the results for α -pinene^{10 11, 44, 57 65}, Δ^3 -carene,⁵⁷ sabinene,⁵⁷ borneol,⁶⁴ camphor⁶⁴ and camphoric acid and camphoric anhydride⁵⁸. Not only so but a *dl*-mixture has the same spectrum as the active form. This is shown by the results of Jatkar and Padmanabhan⁴³ for dipentene and limonene (Table II). The differences which do, in fact, exist are attributed by these authors to impurities in the dipentene. The nature of these impurities, and the evidence for their presence, will be discussed more conveniently later in this paper.

(c) *The frequency associated with certain links*—The danger of placing too much reliance on the constancy of the frequency of a link has been stressed by many authors (*e.g.*, Sutherland⁶¹). The force fields exerted on the link by the rest of the molecule must play an important part in determining its frequency. It is well known, for instance, that a system containing double bonds in conjugation gives a spectrum in which the frequency characteristic of each double bond is considerably lowered. And it is highly probable that other influences may alter the value for a link, although possibly, to a less extent. Many authors have attempted to attribute certain frequencies to particular links and groupings in terpenes and the assignments could be discussed at a length out of keeping with the scope of this paper. The only link which will be considered will be the ethylenic $C=C$ link. This occurs in the majority of the compounds listed in the tables. It is not always bound in the same way in the molecule, sometimes it is in the ring, sometimes it is exocyclic, and sometimes it is conjugated to a second $C-C$ or to a $C=O$ link. Its frequency has been the subject of considerable speculation, especially by the Japanese workers, Hayashi³⁹⁻⁴¹ and Matsuno and Han⁵³. These authors have elaborated a scheme, based on Bourguet's work¹³, whereby all substances containing a $C=C$ link may be looked upon as substituted ethylenes. When only one $C=C$ link occurs its value will depend on how many of the four hydrogen atoms, originally attached to it in ethylene, have been replaced by substituents. Any group, other

than COOH, OH, Cl, and Br, has the same effect on the frequency (1623 cm^{-1}) of pure ethylene. When the molecule contains two $\text{C}=\text{C}$ links, substituted differently but not in conjugation, the appropriate values for each type of substitution will be found in the spectrum. These values are shown below —




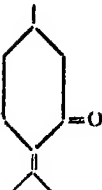

When the $\text{C}=\text{C}$ link is combined with a *cyclohexane* or a *cyclohexene* ring other slight modifications occur



This is applied to the published spectra of certain terpenic compounds, *e.g.*,

Δ^1 <i>m</i> -Menthadiene (Silylmentrene)	Predicted		Found	
	1642,	1675	1630,	1677



Terpinolene		1674, 1675	1668, 1681
Pulegone		(conjugated) 1674, 1714	(19) 1580, 1681 (20) 1617, 1671
Δ^1 -p-Menthene (Carvomenthene)		1675	(22) 1691 (23) 1681 (50) 1681

Hayashi has also applied the scheme to bridged compounds, derivatives of carane, thujane, pinane, and camphane, and he concludes that compounds containing a 1 3-bridge (thujane and pinane derivatives) fall into the scheme but that when a 1 2-(carane) or a 1 4-(camphane) bridge is present the scheme no longer holds. It will have been observed that, for the four compounds for which predicted and ascertained values are given the agreement between them is tolerable but not complete.

Such a scheme would be of immense value if it were applicable to "non-bridged" and "1 3-bridged" compounds. But when it is tested out for all the data contained in the tables, its applicability is less than has been claimed for it. A serious drawback to testing it arises from the influence of conjugation on the value of the $C=C$ frequency. Isoprene, $CH_2=C(CH_3) \cdot CH=CH_2$, has two links in conjugation, one disubstituted, the other monosubstituted. Its spectrum contains only one intense displacement of mean value 1638 cm^{-1} . According to the scheme outlined the two values 1642 and 1653 cm^{-1} , diminished on account of conjugation, should be found. It is, of course, possible that this does in fact occur and that the diminution of one type is greater than that of the other with the consequent overlapping of the two characteristic frequencies. On the other hand, it is apparently impossible to incorporate ocimene, $CH_3 \overset{I}{C}(CH_3) \cdot CH_2 \cdot CH_2 \cdot \overset{II}{CH} \cdot \overset{III}{C}(CH_3) \cdot CH=CH_2$, into the scheme. It gives two displacements

of 1634 and 1666 cm^{-1} whereas it would be anticipated that the displacement 1653 cm^{-1} for the non-conjugated disubstituted link (I) and decreased values (from 1675 and 1642 cm^{-1}) for the tri-(II) and mono-(III) substituted links would be found. All the difficulties encountered in a rigorous test of Hayashi's scheme cannot be discussed in detail here and consideration of it will be terminated by reference to bridged compounds. The claim that the 1,3-bridge has no influence on the characteristic value for a substituted link is not justifiable. To support this claim Hayashi has applied the scheme to

 α -pinene β -pinene

sabinene

Mean Value from Tables	1662	1638	1655 cm^{-1}
Predicted Value	1675	1655	1655 cm^{-1}

It is unfortunate that, in advancing the claim, Hayashi cited only the value of Dupont, Daure and Allard³⁰ for α -pinene, viz, 1672 cm^{-1} . This value is much higher than that obtained by other investigators (1657 – 1667 cm^{-1}). In addition, verbenol, which contains the same link,



CHOH

gives³⁴ 1657 cm^{-1} , whilst α -thujane



gives³⁷ 1642

cm^{-1} . Finally, in this connection, Δ^3 -carene-



and Δ^4 -carene



each give two displacements of approximately 1640 and 1690

cm.^{-1} (see Table VI), whereas, according to the scheme, only one should be expected if the material under examination is pure

Quite apart from the lack of numerical agreement, it is extremely doubtful whether the application of Hayashi's scheme would be expected to predict accurately the $\text{C}=\text{C}$ link frequency of thujane and pinane derivatives. The derivatives of both can certainly be looked on as compounds containing a 1-3-bridge, but there is a very big difference in that pinane contains a *cyclobutane* ring whilst thujane contains a *cyclopropane* ring and thus resembles the carane derivatives which have a 1-2-bridge. It is a well-established fact that the molecular refractivities of bicyclic compounds containing a *cyclopropane* ring show optical exaltation when they have a double bond in conjugation with either of the terminal carbon atoms of the bridge. Bicyclic compounds containing a *cyclobutane* show this to a much less extent. It might, therefore, be expected that this should be reflected in Raman spectra by a depression of the predicted value of the $\text{C}=\text{C}$ link in, for example, sabinene, α -thujene, and Δ^4 -carene. Actually Δ^4 -carene shows a considerable exaltation of the frequency and has the same value as Δ^3 -carene which does not exhibit this "conjugation".

(d) *Detection of the constituents of a mixture*—It is in this connexion that Raman effect would find its most useful application in the chemistry of the terpenes, and it is for this reason that some of the claims made must be considered in some detail. The principal workers in this branch have been Dupont and his collaborators. Most of their evidence pivots round the consideration of the characteristic frequency of the ethylenic $\text{C}=\text{C}$ link but it is to some extent dependent also on the values of other frequencies. All the work from this laboratory is similar in technique. A mixture of terpenes or terpenic compounds is fractionated. For the several fractions various physical constants are recorded. The Raman spectrum of each fraction is determined and a large number of the observed Raman displacements are assigned to possible constituents of the mixture. It is claimed that the assignments are supported by collateral chemical evidence but the present author does not feel competent to express an opinion on the validity of this evidence. It is proposed, therefore, to consider the spectroscopic evidence on its own merits.

Bonichon⁴ claims to have found distinctive differences between the spectra of spatial isomerides, *e.g.*, bornyl and *iso*-bornyl esters (Table VIII), carvomenthol and menthol, and *isopulegol* and dihydrocarveol (Table III), based on the intensities of lines less than 1600 cm.^{-1} . Already a caveat regarding intensities has been expressed in this paper and it is strongly felt that his claims cannot be accepted—nor rejected—until independent

confirmation of his experimental data has been obtained. Yet, on examining the data (Table VIII) for the esters of borneol and isoborneol, the assertion of Bonichon that the spectra of these esters are very different is not strongly supported. Consequently, it is rather doubtful if Raman spectral methods would be serviceable at present in detecting these isomerides in a mixture.

Bourguel and Piaux¹⁴ stated in 1931 that they could detect the presence of isoprene as an impurity in dimethyl-1,1-allene, without mentioning the reference lines of isoprene on which they base their claim. Later Gehman and Osterhof²⁵ consider that it is possible to detect not less than 5 per cent isoprene in trimethylethylene because of the appearance of a weak $C = C$ displacement at 1640 cm^{-1} . This is conceivable. But it must be remembered that these molecules are much less complex than terpenic molecules and, accordingly, have simpler spectra. A large number of papers—too large to examine in detail here—dealing with the detection of isomerides in a mixture of terpenes have appeared. Not only so but Dupont and his collaborators have claimed to establish the occurrence and constitution of some hitherto unknown compounds, as well as to establish the existence of certain (five in number) unidentifiable terpene analogues or isomers. And actually, from the Raman spectrum of American wood turpentine, Dupont, Rambaud, and Bonichon²⁶ give the following composition to the turpentine: α -Pinene 76, Limonene 9.8, α -Terpinene 8.2, β -Pinene 4 (?), Terpinolene 2%, and γ -Terpinene in traces. Spectroscopically these quantities are almost certainly unjustifiable.

In Table VI the spectra of two fractions containing Δ^2 -carene are given. Fraction 19 shows the two displacements $1640\text{ (an } \delta)$ and $1690\text{ (n } \delta)\text{ cm}^{-1}$, fraction 27 gives $1640\text{ (f } \gamma)$ and $1690\text{ (n } \delta)\text{ cm}^{-1}$. From this it is reasoned that 1640 cm^{-1} must originate from an impurity containing an exocyclic $C = C$ link and present in greater amount in fraction 19 than in fraction 27. This impurity could be β -pinene but this is ruled out because no other characteristic displacements of β -pinene are observed. (Comparison with the data in Table VII for β -pinene makes this statement debatable.) It is concluded that the impurity must be an isomeric carene with an exocyclic $C = C$ link,

called β -carene and presumably representable as



. The validity

of such a claim, from a spectroscopic standpoint is very slender.

The existence and constitution of a new type of terpenes, called pyrenenes ($C_{10}H_{18}$), have been postulated by Dupont and Dulou^{24, 25} in the pyrolysis products of pinene. The independent chemical evidence on the structure of these hydrocarbons is still slender and requires confirmation.

In several papers reference is made to chemically unidentifiable terpenes. For instance, Dupont and Gachard²⁶ report that in the spectra of 54 fractions of non-polymerised pinene, obtained by the isomerisation of pinene by 50 per cent sulphuric acid at approximately 50°, four unidentifiable hydrocarbons X, Y, Z, and T are encountered. These have been characterised by the frequencies X 1634, Y 1661, Z 1514 and 1556, and T 1702 cm^{-1} . The intensities of these displacements are never very great and consequently, the accuracy of measurements cannot be very high. One of the products confirmed in certain fractions by chemical and spectroscopic methods, is camphene, which is characterised by the frequency 1658–1663 cm^{-1} . Is it not possible that Y may be camphene even though tests for camphene were negative? In the same paper many displacements are assigned to α - and γ -terpenines and to terpinolene, these assignments comprise all the available information regarding the spectra of these compounds and are listed in Table II. Such a procedure of *deducing* the spectra of compounds by examination of complicated mixtures of uncertain composition is quite unjustifiable. The spectroscopic evidence for the presence of these compounds in mixtures is not acceptable unless comparison with the spectra of the pure substances is possible. The same criticism can be levelled at the results for the dehydration products of commercial terpineol²⁸ in which the existence of the terpenines, terpinolene, and the unidentifiable compounds T, Z, and U (1608–1610 cm^{-1}) is postulated. (It may be significant to point out that α -terpinene is identified by the frequency, 1610–1614 cm^{-1}).

It is not possible to give a detailed discussion of the other work from Dupont's laboratory. Generally speaking the criticisms given are applicable to the whole of it and particularly to the other papers^{24, 25} dealing with the analysis of mixtures.

There is a lack of accurate—and verified—data on terpenes and terpene derivatives. Until such data become available the results on the spectroscopic examination of complicated mixtures must be considered as untrustworthy. Even when such data do become available they must be supported by rigorous chemical and physical criteria of purity. The present position is thus somewhat nebulous. For instance, Jatkar and Padmanabhan²⁸ conclude that because their spectrum of dipentene contains frequencies, attributed by Dupont and Gachard²⁶ to α -terpinene and terpinolene,

these are present as impurities. It has already been noted that, for these substances, no reliable spectroscopic data exist. Therefore, although from chemical standards these are likely impurities, it must be repeated that the spectroscopic evidence of their presence is quite unacceptable.

The dangers inherent in attempting to analyse mixtures of terpenic compounds are indicated by Snitter's work⁵⁹ on camphenylene. By the methods of Raman spectra he concluded that the hydrocarbon which he examined was pure camphenylene contaminated by 2-5 per cent apobornylene, but containing no santene. Chemical evidence has been adduced by Gratton and Simonsen,⁵⁷ by Komppa and Nyman⁴⁸ and by Lipp⁶¹ which proves that this hydrocarbon is essentially apocyclene and santene.

Summary

The available Raman spectral data on terpenic compounds are tabulated and reviewed. It is concluded that the identification of the constituents of a mixture of terpenes by Raman effect methods cannot give trustworthy results until confirmatory results on possible constituents have been obtained.

Acknowledgements

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TABLES

TABLE I
Acyclic Terpenes and their Derivatives

(Isoprene)		Myrcene	Ocimene	Allo Ocimene	Geraniol	Linalool	Citronellol		α -Citral	Citronellal		Citronellic Acid
(15)	(16)	(60)	(80)	(25)	(8)	(8)	(8)	(56)	(8)	(8)	(56)	(56)
200(f)	200(1)			145(3)		310(1)			290(2) 351(1)	351(1)		
422(f)	422(2)		473(1)	442(2)	456(4)	456(2)	456(2)		466(1) 510(1)			
530(m)	530(4)	125 4(4)				351(1)						
770(f)	770(2)		752 8(4)	791(f 2) 843(f 2) 871(4)	816(1)	754(0)	780(2) 814(2)			756(2)		
801(m B)	800(3 b)	809 8(8)								836(2 d)		867 7(f 1) 851(f 1)
903(f)	954(4)	950 8(1)	939 1(2)	953(f 2) 906(f 8)		928(4)				930(1) 943(3)		956(mf 1)
905(f)	904(2)	904 1(1)		1025(f 3)	1016(3 d)		990(2)		995(1)	1035(0)	981(f 1)	1028(f 1)
1070(m)	1070(4)	1066-6(4)	1069 5(1)				1096(3 d) 1103(2)			1090(2 d) 1123(1)	1077(f 2) 1087(f 1) 1105(f 2)	1084(mf 1)
				1131(15) 1185(15) 1180(1) 1233(1)				1110(f 2) 1140(f 1)				
			1235 3(3)	1273(8) 1307(15)							1233(f 1)	
1290(f)	1291(5)	1292-5(5)	1285 3(1)			1292(4)		1295(f 1) 1323(f 2)	1328(2)		1295(f 1) 1323(f 1)	1295(f 1)

1388(f)	1380(1)	1382 3(1)	1381(6)	1344 4(1)	1345(3)	1384(2)	1387(3)	1346(f 2)	1342(0)	1343(f 1) 1348(f 3) 1382(n 8)	1382(n 5)
1426(a,f 5)	1420(5)	1422 4(3)	1424(6)	1406 1(1)	1434 1436 1438 1439	1434 1436 1438 1439	1437(5)	1434 1439	1452(1)	1439 1459	1439 1465
1640(TF)	1636(10)	1638 8(10)	1638(15)	1634(7)	1630 1631	1675(5)	1672(5)	1677(n 12)	1675(3) 1719(2)	1677(n 13) 1729(f 6)	1653(f 1) 1679(n 12)
2864(F)	2820(2)	2814 3(3)	2814(12)	2812(1)	2852(6)	2859(3)	2893(7)	2891(3)	2891(5)		
2908(m)	2900(m)	2901 2(2)	2905(2)	2903(1)	2918(5)	2918(5)	2923(3)	2968(2)	2959(3)		
2986(m)	2987(1)	3015 7(5)	3004(6)	3055(1)							
3012(F)	3010(5)										
3090(a,F)	3083(3)	3092(2)	3083(6)								

TABLE
Monocyclic Terpenes and Some

Limonene							α Phellandrene		α Terpinene
(7)	(22)	(23)	(43)*	(43)	(50)	(60)	(22)	(23)	(26)
316($\frac{1}{2}$)	304(f3)	308(an1) 330(an2)					258(f1) 289(f1) 314(f1)		
	350(f3)	350(f1)					376(B2)		
433(1 $\frac{1}{2}$)	437(f2)	432(an2)	423(1b) 447(1b)	429(1)	434(f)		437(B2)		
(409)(1) 503(0)	497(f1)	471(f1) 491(f2)		487(0)	497(f)				
525(1) 552(1)	528 553	524(an4) 544(an2)	509(1b)	516(1)	526(f) 548(f)				
			569(1b)						
643(0)	648(B2) 677(B1)	639(n2) 662(n1)	633(2b) 668(2b)		638(f)	635 7($\frac{1}{2}$)	603(B2) 643(B1)	581(f1) 599(f1)	581(f1)
711(0)	707(B2)	702(f2)	706(2b)	702(2b)		673 7($\frac{1}{2}$)		667(f1)	644(B2)
765(3)	766(n8)	757(an10)	754(4)	755(5)	766(nF)	713-7($\frac{1}{2}$)	707(an2)	709(an3)	
802(2)	810(an4)	790(an4) 800(an4)	795(1) 807(1) 816(1)	788(2b)	801(m)	760-1(3)		769(f1) 786(an3)	
						818-5($\frac{1}{2}$)	815(B4)		
899(1)	894(an3)	895(f3)	872(4)	884(2) 912(1)	896(m)	879 2(3)		854(f1)	880(f4)
916(1)	918(an1)	918(f2)	919(1) 934(1) 948(1)		927(f)			934(B3)	
950(1) 963(0)	961(f1)	956(f1)			956(f)		957(B3)	969(B3)	
1010(0)	1019(B3)	995(f1) 1020(B2)	1013(0)	1018(1)	1024(f)		1019(B3)		

* Dipentene.

II

Related $C_{10}H_{16}$ and $C_{10}H_{18}$ Compounds

γ Terpinene	Terpinolene	$\Delta^1 s m$ Menthadiene (Sylvestrene)	$\Delta^1 s$ or $\Delta^3 s$ $\Delta^3 m$ Menthadiene [†]	$\Delta^1 m$ Menthene	$\Delta^2 m$ Menthene	$\Delta^1 p$ Menthene (Carvomenthene)				$\Delta^2 p$ Menthene
(26)	(26)	(23)	(36) [†]	(23)	(36) [‡]	(7)	(22)	(23)	(50)	(5)
6457(n4)	6077(n4) 6437(n4) 727(n7)				22(f)	143(1)				
			333(fff)			298(2)	294(f1)	322(f1)		
		339(an2)					339(f1)			
		364(f1)	356(F)		381(fff)				371(f) 411(f)	
		429(?)	437(ff)	421(f1)	422 5(ff)	418(1)		416(f1) 435(f1) 442(f1)	432(f)	442
		450(?)		449(?)			447(B1)			
		473(?)	462.5(ff)					493(an1)		
		492(?)								
					525(F)		528(B1)	522(f1)	517(f)	
		555(?)	553(F)					553(f1)		
		6077(n4)	603(F)							
		626(n6)	648(f)	627(an4) 646(f1)	640(aF)					
		719(B1)			732(fff)	753(4)				
			752(fff)	752(an2)			766(n6)	764(an8)	766(F)	
		782(f3)		774(an3)	791(F)			784 (an3) 799	801(f)	
		830(?)	820(fff)	820(f1)			810(an3)			
				867(?)		873(1)	859(an2)	858(f3)	834(m)	
		879 } 899 } (B4)	884(fff)	880(?)						
		935(f1)		921 } 929 } (B1)			918(f2)	918(f2)	908(f)	
			957(F)	953(f1)	957(F)	948(2) 959(1)	961(f2)	952(f3)	954(f)	962
		1004(f2)	995(f)	1003(?)	1000(f)				1005(f)	
							1010(B1)	1013(B1) 1019(f1)		

[†] Mixture of $\Delta^1 s$ and $\Delta^3 s$ $\Delta^3 m$ Menthadiene[‡] Mixture of $\Delta^1 s$ and $\Delta^3 s$ $\Delta^3 m$ Menthene

TABLE

Limonene							α -Phellandrene		α -Terpinene
(7)	(22)	(23)	(43)*	(43)	(50)	(60)	(22)	(23)	(26)
33(0)		1054(f2)			1062(f)	1051.5(B $\frac{1}{2}$)	1037(B1)		
68(0)				1074(0)					
88(0)	1082(an1)	1080(an3)	1096(2b)	1103(1b)	1084(f)			1115(B2)	
		1115(an3)			1121(f)				
23(0)	1129(an1)				1158(m)		1139(B1)		
		1155(ar 5)	1148(1b)	1153(3b)					
68(1)	1168(n3)						1177(B1)	1172(f4)	
		1205(B1)	1205(2)	1198(1b)	1205(1 f.)	1207.9(3)	1219(an3)		
113(0)	1215(an1)		1227(2)	1239(1b)					1238*(f3)
151(0)					1247(f)				
188(0)	1257(an1)								
113(0)	1290 } (B2)	1293(f2)	1293(2b)	1279(1b)	1290(f)	1306 9(2)			
	1327 }	1311(f2)		1306(1b)	1318(f)				
		1333(f2)							
178(2)	1379(B4)	1368 } (B5)	1369(3b)	1368(5b)	1374(m)	1375(2)			1384(f1)
		1380 }						1406(an3)	
		1397(f2)						1439 }	1430 }
446(5)	1434 }	1435 }	1429(3)	1430(8)	1434 } (F)	1440 2(2)		1448 }	
	1471 }	1455 }	1444(2)		1453 } (m)		1467(B4)	1467 }	
			1506(2)						
			1549(9)						
			1607(10)						
658(3)	1641(n4)	1647(an15)	1637(3)	1643(10)	1645(F)	1610.6(6)	1600(B6)	1591(an10)	1615.4(an15)
		1667(an15)	1658(3)				16317(an3)	1640(an8)	
690(3)			1677(3)	1678(10)	1681(F)	1673(B1)	16817(an3)		
	1691(n8)								
			2667(0b)						
			2722(0b)						
			2820(1b)						
1900(4)		2834(f2)		2832(2bb)	2835 } (aF)	2868.5(2)			
		2859(f1)	2867(4b)		2882 } (aF)				
					2916 } (F)	2922(2)			
1923(4)		2908 } (B4)	2914(4b)	2915(5bb)	2931 } (F)				
		2924 }							
2973(3)		2904(f2)	2907(4b)	2959(1bb)	2968(m)	2971 5(2)			
				3009(0)	2981(f)				
3082(2)		3048(an.2)	3047(4)	3044(8)	3018(f)				
				3083(0h)	3082(f)				
3156(?)									

* Dipentene.

II (Contd.)

γ Terpinene	Terpinolene	Δ^1 s m Menthadiene (Sylvestrene)	Δ^2 or Δ^3 s -m Menthadiene	Δ^1 m Menthene	Δ^2 m Menthene	Δ^1 p-Menthene (Carvomenthene)				Δ^3 Menthene
(26)	(26)	(23)	(36) †	(23)	(36) ‡	(7)	(22)	(23)	(50)	(5)
1376(B6)	1228(an10)	1064(?)		1063(?)		1088(3)		1062(B2)	1038(f)	1063
		1110(?)		1109(?)				1104(B2)	1072(f)	
		1152(?)		1164(?)	1171(f)		1163(B3)	1156(B3)	1110(f)	
			1171(ff)	1190(?)					1158(m)	
			1219(F)	1215(?)	1219(f)		1243(B2)	1221(f1)	1218(tf)	1448 1521 1536
								1272(?)	1247(tf)	
		1286(an3)	1282(F)			1291(3)	1299 } (B3)	1294 (f2)	1290(m)	
		1321(an2)		1332(f1)			1327 }	1310(an3)	1313(aF)	
		1377(f5)	1360(F)	1371(f2)		1378(1)		1361(f1)	1374(aF)	
		1434(f10)		1427 } (B8)	1440(F)		1434 } (B10)	1372(f4)	1420(F)	
		1457(f7)	1444(TF)	1459 }		1450(5)	1471 }	1429(f10)		
								1444(f8)	1402(m)	
								1464(f4)		
1638(n10)	1668 } (10) 1661 }	1639(an9)	1630(T F)		1600(f1)					2846 2923 3041
		1677(an8)		1676(an6)	1675(F1)	1673(4)	1691(n8)	1681(an8)	1691(F)	
		2835 } (B3)		2836(f4)		2867(5)		2831(f1)	2833(m)	
				2871(f6)				2874(B3)	2871(aF)	
		2911 } (B4)		2908(B4)		2918(5)		2917(f2)	2921(F)	
				2930(an6)		2934(5)				
		2943 } (B2)				2962(5)		2952 } (B2)	2968(m)	
		2964(f3)						2964 }		
		2984(f1)		3045(?)		3074(1)			3015(F)	
		3048(an1)								
		3075(an2)								
		3094(an1)		3119(an1)		(3146)(2)				
		3126(f3)								

† Mixture of Δ^1 s-s- and Δ^2 s-m-Menthadiene‡ Mixture of Δ^1 and Δ^2 -m-Menthene

TABLE
Alcohols and Esters

α Terpinol			α Terpinyl Acetate	β Terpineol*	Iso Pulegol	Iso Pulegyl Formate	Iso-Pulegyl Acetate
(54)	(4)	(47)	(4)	(8)	(4)	(4)	(4)
194(1 bbd)	182(f 2)		182(f 1)		170(f 2)	170(f 2)	170(f 2)
	260(f 1)		260(f 1)		237(f 1)	237(f 1)	237(f 1)
	295(f 2)	280(2)		294(2)	298(an 6)	292(f 1) 309(f 5)	296(f 1)
323(3 d)	325(f 1) 375(f 1)	318(1) 368(1 b)	310(f 1)	324(1) 373($\frac{1}{2}$)			321(f 5)
					399(an 2)	399(f 2)	399(f 1)
434 (4)	430(f 2)	429(1)	413(f 1) 436(f 2)	433($\frac{1}{2}$)	428(an 2)		
455($\frac{1}{2}$ d)					458(an 2)	442(f 1) 458 } (B 2)	442(f 1) 458(f 1)
	470(f 1)		470(f 1)		468(an 2)	468 }	468(f 1) 473(f 1)
495($\frac{1}{2}$ d)	509(f 3)	502(2)	509(f 2)	512(2)		512(an 3)	
518(3)					528(an 3)	528(f 2)	528(an 3)
546($\frac{1}{2}$)	545(f 3)	543(3)	545(f 2)			542 (f 1)	542(f 1)
($\frac{1}{2}$ d)				550(2)	552(an 2) 583(f 1)		
			612(f 1) 630(f 1)				633(f 1)
651(3)	643(f 2)	639($\frac{1}{2}$ b)	659(f 1)	642(1)	667(f 1)		656(f 3)
683(3)			677(f 1)				
732(8)				725(3)	717(f 1)		
765($\frac{1}{2}$ bd)	756(an 10)	758(7)	756(an 10) 771(f 1)	761(5)	775(an 10)	761(an 4) 775(f 1)	775(an 8)
	778(f 3)					794(f 3)	
802(4 bd)	803(f 1)	801(1)	801(f 1) 810(f 1)		819(f 1)	819(f 2)	819(f 2)
		832(2)					
839(1 d)					845(f 1)	845(f 1)	
864(3 d)	867(f 2)		867 }				
			(B 1)				
890(5)	898(f 1) 913 }	917(2)	898 913 }		891(f 3)	891 (f 4) 913(f 3)	891(f 3) 913(f 1)
	(B 5)						
928(2)	928 }		944 }	922(3)	925 } (B 1) 939 }	925(1) 939(1)	939(f 2)

* Mixture of a and b terpineols

III.

of Monocyclic Terpenes

Dihydro-carveol	Carvomenthol	Menthol	Menthyl Formate	Menthyl Acetate		1 8 Cineol
(4)	(4)	(4)	(4)	(4)	(54)	(8)
170(f 2)		182(f 1)	182(B 3) 193(?)	182(f 1)		
222 } (B 1)					230($\frac{1}{2}$)	220(0)
243 }		260(f 1)	241(f 2) 260(f 1)	260(f 1)		253(4)
287 } (B 2)	286(f 1)	291(f 2)	289(f 5)	291(an 1)	293(?)	305(2)
310 }	317(f 2)		316(f 2)	316(an 1)	318(3)	
		409(f 2) 427(f 2)	409(f 5)	387(f 1) 409(f 2)	(409)(3) (424)(0)	391(1)
445(f 1)			449(f 2)			
464(f 1)		466(f 1)	466(f 2)		465(2)	461(3)
502(f 2)	496(f 2) 512(f 2)	503(f 4)	506(f 3) 529(f 2)	503(f 2)	504(3)	518(1)
		551(f 1)	549(f 1)	538(f 1)	544(4 d)	558(3)
		600(f 1)	598(f 1)	598(f 1)	596(2)	603(0)
				640(f 3)	651(3)	665(7)
704 } (B 1)					(717)?($\frac{1}{2}$)	
732 }	752(an 10) 771(an 6) 783(f 1) 792(f 1)	771(an 10)	755(an 10) 771(f 1)	771(an 10)	768(5) 778(6)	
773(an 5)		793(f 1) 806(f 4)	793(an 8) 806(an 6)	793(f 1) 806(f 3)	809(4)	
827(f 1)	830 } (B 1)	846(f 4)	842(f 1)	846(f 1)	846(2)	825(?)
	864 }	875(f 3)		875(an 4)	875(5)	870(?)
	875(f 1)		885(f 3) 908(f 3)	903(f 1)	(905)(2)	
893(f 4)		922(f 4)	922(f 3)	922(f 2)	(924)(1) 930(1)	933(3)
920(f 1)						

TABLE

α Terpinol			α Terpinyl Acetate	β Terpinol*	Iso Pulegol	Iso Pulegyl Formate	Iso Pulegyl Acetate
(54)	(4)	(47)	(4)	(8)	(4)	(4)	(4)
951(5) 962(1 d) (990)(2)						967(f 2) 992 } (B 3)	967(f 1) 992(f 1) 967(f 1) 992(f 2)
1027(2 b)	1021(f 4)	1010(2)	1021(f 3)	1025(2)	1006 1029(f 3) 1044(f 3) 1053(an 3)	1006(f 1) 1029(f 1)	1006(f 1) 1048 (f 3)
1051(2) 1073(6) 1073(6) 1096(1)	1060(f 2) 1081(f 4) 1117(f 2)	1078 } (3 ab)	1053(f 2) 1081(f 3) 1117(f 2)	1089(2)	1085(f 1) 1119 1129 } (B 6)	1052(f 4) 1085(f 4)	1085(f 2)
1131(8 bd)		1145	1148 } (B 3) 1158 1184(f 1)	1143(3)		1136(f 4) 1170 } (B 5) 1186 1217(f 1) 1235(an 4)	1138(f 5) 1170(f 5) 1217(f 1)
1163(6 d)	1163(B 5)						
1250(5 d)	1220(f 2) 1251(f 3)	1244(2 b)	1220(f 1) 1249(f 3)	1239(1)	1279 } (B 2) 1295 1310(f 2)	1235(an 4)	1290(f 1) 1310(f 1)
1312(6bbd)	1301 } (B 5) 1315 1327(f 2)	1295(4)	1301(f 1) 1315(f 3) 1327(f 1)	1317(1)	1351(f 8)	1310(f 1)	1310(f 1)
1371(6 d)	1362 } (B 4) 1382	1366(4)	1360 } (B 4) 1382	1384(2)	1403(f 4) 1433 } (B 4) 1453 1459(an 12)	1351(f 4) 1360(f 2) 1384(f 2) 1403(f 3) 1435(f 5) 1453(f 5) 1459(n 10)	1351(f 3) 1360(f 2) 1384(f 2) 1403(an 3) 1433 } (B 8) 1453 1459(n 10)
1428(6) 1449(6)	1432 } (B 8) 1452	1438(8 b)	1432 } (B 15) 1452	1449(4)	1645(an 12)	1645(n 15)	1645(n 10)
1468(4)	1467					1715(f 3)	
1682(8)	1681(n 8)	1673(5)	1681(n 10) 1739 ?(f 1)	1673(3)			1740(f 3)
2832(2 d) 2849(6 b) 2879(6bbd)		2844(3 b) 2875(3 b) 2917(4 b)					
2932(6) 2961(3) 3020(1)		2970(1 b)		2925(5) 2956(3)			

* Mixture of a and b terpinols

III (Contd.)

Dihydro carveol	Carvomenthol	Menthol	Menthyl Formate	Menthyl Acetate		1,8 Cineol
(4)	(4)	(4)	(4)	(4)	(54)	(8)
952(f 1) 971(f 1) 987(f 1)	958(an 7)	956 } 980 } (B 4)	956(f 4) 980(f 4)	956(f 2) 980(f 4)	(954) (3) 975(3)	
	1002(f 1)	1000(f 4)	1010(f 3)	1000 } 1014 } (B 2)		1033(2)
1044(f 1) 1057(f 1)	1039(an 1) 1063(f 4)	1046(an 8) 1079(f 3)	1041(an 5) 1057(f 2) 1079(f 3) 1099(f 3)	1041(an 8) 1057(f 2) 1079 } 1099 } (B 4)	1042(4) (1062)(4) 1081(6 bd)	1098(0)
1110 } 1149 } (B 1)	1152(f 4) 1178(f 2)	1148(f 1) 1181(f 8)	1148(f 3) 1181(f 8)	1150(f 5) 1181(an 8)	1150(6 bbd) 1163(6 bbd) 1184(6 d)	1121(2) 1166(6)
	1261(f 3)	1245(an 3) 1270(f 2)	1245(an 5) 1270(f 4)	1245(an 5) 1270(f 3)	1242(5) 1271(4)	1230(1) 1280(2)
		1310(f 1) 1327(f 1) 1350 } 1370 } (B 2) 1379 }	1310(f 2) 1327(f 3) 1350(an 4) 1370 } 1379 } (B 4)	1310(f 1) 1327(f 1) 1350(f 3) 1371(f 3) 1379(f 3)	1317(3) 1381(4d)	1303(2) 1409(0)
1433(f 5) 1459(f 5)	1434 } 1470 } (B 13)	1440 } 1467 } (B 12)	1440 } 1467 } (B 8)	1440 } 1467 } (B 8)	1443(5) 1467(6 d)	1452(5) 1480(1)
1645(an 10) 1679(f 1)			1725(f 3)	1739(f 4)	1737(2 d) 2818(6bd) 2870(6 bbd) 2930(4 d) 2968(6 d)	2925(5) 2971(5)

TABLE V *Thujane and its Derivatives*

Thujane	α Thujene	Sabinene			β Thujene	
(6)	(57)	(6)	(54)	(57)	(8)	(19)
			(120)(3bd) (169)(2bd) (214)(1)			
312(2)	(299)(1) (335)(1) (372)(1)	308(1) 373(2)	306(3) 333(1) 362(3d) (373)(1)	(265)(1) 317(2) 370(2)	269(2) 313(3)	256(f3) 306(f10) 338(f7) 362(f6)
						396(f1) 416(f6) 459(f1) 474(f3)
443(2) 479(0) 493(1)	497(1)	448(2)	441(3)	448(2)	434(1)	
559(2)	553(1) (621)(1)	503(2) 573(0) 645(3)	491(1d) 509(3) 566(2) 634(1)	503(2) 570(1) 641(3)	496(1)	
669(3) 693(1)	670(1)		655(5)			
	732(3)				720(1) 758(4)	712(f7) 751(f15) 820(f12)
768(5) 808(0) 839(1) 867(1)	807(3) 843(1)	781(1) 808(2)	785(5) 808(4d)	789(2) 815(2)		
		863(3)	866(4bd) 882(2d) 915(2) 930(1) 954(6bb) 989(3)	869(3) 921(2)	832(1) 877(3)	867(f12)
953(4)	947(1) 979(1)	903(3)		903(3)	950(3) 973(1)	942(f15) 971(f12) 1014(f15) 1039(f12) 1065(f15) 1085(f13) 1123(f12) 1133(f6) 1153(f5) 1174(f5) 1213(f5)
1015(2) 1041(0)		1039(2)	1031(5) 1067(4) 1109(6bd)	1036(3)		
1103(1) 1123(3)		1103(1) 1123(1)		1112(2)	1133(5)	
		1155(0)	1145(4d) 1170(3d) 1197(6) 11214(1d)			
1183(2) 1218(1)	1168(2) 1210(1)	1212(1)		1209(3)		
1291(0) 1305(0) 1318(2) 1383(2)	(1274)(1)	1270(0)	1270(4bd)	1276(1)	1262(1)	1240(f5) 1259(f5)
		1308(0) 1385(0) 1421(8)	1308(4bb) 1379(3d) 1415(8) 1438(4d) 1447(5d) 1468(4d)	1311(3) 1425(3)	1320(1)	1312(f5) 1384(f7) 1413(f8)
1453(5)	1445(3)	1448(4)		1456(3)		1446
1663(1)	1642(3)	1656(5)	1656(10bd)	1653(5)	1470(4)	1471(f13) 1637(f4) 1682(f4) 1747(f12)
			2830(4)		1688(2) 1750(3)	
2869(5)	2875(2) 2910(3)	2878(4)	2913(2)	2875(3)	2875(3)	
2923(4)		2918(4)	2940(2)	2923(3)		
(2950)(12) 2964(5)		2963(4)	2964(6) 2966(4bd)		2940(1)	
	2960(3) 3050(2)	2966(2) 3043(3) 3076(3) 3152(1)	3070(4b)	3090(3) 3040(1)	2966(3)	
(3139)(2)					3067(4)	

TABLE VI
Carane and its Derivatives

Carane (20)	Δ^3 -Carene				Δ^4 -Carene (57)
	(20)	(27) Fraction 19	(27) Fraction 27	(57)	
					311(1)
424(B4)	355(f2)	350(f2)	356(f2)	353(2)	
	432(f3)	432(f2)	427(f3)	424(2)	415(1)
		467(f1)			485(1)
527(f1)	517(f4)	507(f2)	517(f4)	513(1)	517(2)
568(f1)	573(f3)	573(f2)	568(f3)	573(2)	
682(an4)	682(an4)	677(an4)	677(an4)	683(2)	670(2)
					704(2)
727(an2)	727(n6)	722(n6)	722(n6)	719(3)	
	766(an3)	761(an2)	761(an3)	761(2)	758(3)
	796(an1)		791(an1)		
	825(an4)	20(an3)	820(an4)	825(2)	831(2)
					862(3)
					908(1)
	947(n6)	947(n6)	942(n6)	940(1)	958(3)
					988(1)
					1067(2)
1120(B2)	1105(f1)		1100(f1)	1111(3)	
					1141(2)
	1163(f2)	1158(f2)	1158(f2)	1162(2)	
1181(f1)					1216(1)
1234(f1)	1229(B1)	1234(f2)	1224(f1)	1231(2)	1258(1)
1309(f2)	1313(an4)	1308(B2)	1308(an4)	1311(1)	1304(2)
					1333(1)
1363(B2)	1383(n6)	1378(an4)	1378(an6)	1377(2)	1397(2)
					1420(1)
1434 } (B10)	1430 } (B10)	1425 } (B8)	1442 } (B10)	1438(4)	
1471 }	1400 }	1457 }	1449 }		1448(5)
	1568(f2)		1563(B2)		1554(2)
	1645(f1)	1640(an4)	1640(f1)	1641(1)	1639(1)
					1670(3)
	1695(n8)	1690(n8)	1690(n8)	1684(3)	
				2834(2)	
				2876(3)	2876(3)
				2918(3)	2918(4)
				3008(2)	3008(3)

Pinene		α -Pinene							β -Pinene				
(6)	(20)	(11)	(5)	(6)	(18)	(20)	(27)	(54)	(57)	(65)	(20)	(27)	(48)
		134(2)		123(2)	139			134(3bd)	146(3)	134(3b)			
		205(2)		213(1)	207	222(B2)	217(an2)	(208)(2bd)	210(1)	213(0d)			
		260(2)		266(3)	256			261(3d)	265(3)	261(2)			
306(0)		309(1)		308(0)	307	278(an4)	273(an4)	306(2d)	314(1)	306(0)			306(2b5)
		335(1)			335	309(f2)	304(ab2)	(333)(0)					327(2b5)
306(1)		368(1)		392(2)	389	391(f3)	386(an2)	388(3bd)	395(1)	388(2)	391(f1)		382(1b5)
		423(1)			394			(426)(2)	428(1)	428(0)			
478(1)		465(1)		478(1)	467	477(bf2)	472(B2)	(465)(2)	480(2)	476(0b)	480(n2)	471(f1)	482(2b5)
		494(1)			483			(489)(3)					488(2b5)
		568(1)		565(2)	565	573(n4)	568(n4)	564(4)	574(3)	564(2)			562(2a)
600(4)		623(1)	644	619(1)	613	623(n3)	618(n3)	620(3)	626(2)	620(1)	648(tn5)	643(an5)	639(an)
		668(5)		673(5)	668	672(tn7)	667(tn7)	667(6)	670(4)	647(0)			
704(2)	752(5)	774(2)		778(2)	771	778(3)	771(f3)	774(4)	779(3)	774(2)	778(3)	771(an1)	712(3b)
					789								
814(2)		823(1)	812		820			822(2)	848(3)	816(0)	850(n5)	845(an2)	813(2)
808(3)	804(1n7)	849(3)	853	847(3)	845	840(n5)	835(an5)	844(5)		844(2)			845(2b)
					889			885(1)	906(1)	878(0)	878(n5)	879(an5)	873(3b)
		908(1)			908			905(3)		904(1)			918
		924(1)			920			930(1)	953(3)	931(0)	942(f7)	937(B2)	921(2b)
948(3)	967(B4)	956(2)	961	968(2)	952	962(B5)	957(B5)	953(3bd)		949(0)			948(2b)

[illegible]

Myrtanol	Verbenol	Myrtanol	Acetate	Isa-Myrtanol	1,2-O-Myrtanol	Acetate	Myrtanal	Nopinone	Verbenone	Camphore	Acetone
(31)	(54)	(30)	(30)	(30)	(30)	(30)	(31)	(19)	(19)	(19)	(66)
	141(4)						102 } (55) 118 }	180(f1)	117 134		143 (B2) 161
	(204)(3)						168 } (f3) 175 }			190(f1)	202(f1)
258(f4)										211(f1)	233(f1)
	(3)(3)(2)		311(f1)				268(n5)	263(f1)	251(f3)	286(f1)	267(f1)
	402(2)	308(f2) 379(f2)	387(an2)	355(f2)			374(n3) 389(n2)	352(f2) 388(f2)	376(f4) 391(f2)	351(f1) 371(f1)	356(f1) 388(f1)
404(an3)	(470)(1)						411(n5)	432(f3)	416(n5)	396(f1)	424(f1)
490(an3)	517(2)	535(f2) 549(f1)	530(f2) 534(f1)				441(n5) 460(n3)	472(f2) 477(f3) 507(f1) 546(f2) 569(f2)	444(n4) 462(f3)		
600 } B3 626 }	614(2)							609(f2)	570(n10) 570(n5)	544(f4) 562(f1) 580(f1)	544(an2)
636(an4)	651(1)	653 } (f5) 666 }				646(n4) 661(f3) 678	631(n4)	652(c10)	623(n12)	657(f3)	
684(an5)	(689)(1)		666(f1)				695(n4)		894(f3)	698(f6)	895(f1)
	730(2)										
782 } (B4) 788 }	777(3)			771 } (B3) 796 }			777(n3)	753(n4) 784(n3)	746(n2) 758(n2)		788(f3)
821(n4) 845(n8)	(799)(1)							824(f3)	802(f2) 823(f9) 840(n8)	812(f2) 836(f2) 850(f3)	820(f1) 842(an1) 857(an1)
864(an3) 906(an3)	843(2d)			861(n10)		859(an4)	885(n3) 906(n3)	863(f7) 874(f3)	889(f2)	893(n3) 907(n3)	901(n7) 919(f1)
								916(f3) 921(n3)	912(f2)		
900 } (B6) 962 }	(925)(3d)						933(n3) 945(n3) 963(n6)	955(f3)	941 } (f4) 949 } 967(n10)	930(f2) 960(f1)	957 } (B5) 960 }

Shane	Camphene	Bornyl	Bornyl Formate	Isobornyl Formate	Bornyl Acetate	Isobornyl Acetate	Bornyl Propionate	Isobornyl Propionate
1)	(20)	(64)	(4)	(4)	(4)	(4)	(4)	(4)
1)	237(B3) 287(an3) 437(f2) 643(n6) 672(n6) 825(f1) 889(an6) 932(an7) 966(f4) 1053(B3) 1115(B3) 1210(B1)	170(f1) 223(f1) 236(f2) 258(f2) 270(f1) 306(f1) 337 } 345 } 360 } 376 } (B1) 389(f4) 434(f1) 467(f1) 501(an5) 526(f2) 586(f3) 600(f5) 655(n10) 729(f3) 763(f2) 822(f5) 840(f2) 881(n4) 913(an4) 937 } (B6) 961 } 973 } (B4) 990 } 1007 } (B3) 1031 } 1048(B) 1083(an6) 1114(f4) 1147(B3) 1160 } (B8) 1207 } 1230(f7) 1257(f4)	182 } 201 } (B2) 237(f3) 266 391(f2) 402 466(f1) 514(f1) 527(f1) 573(f1) 593(an6) 627(n8) 641(an10) 654(an10) 747(f2) 781(f2) 824(f2) 835(f2) 888(f3) 906(f3) 921(f3) 937 } (B5) 962 } 982 } (B1) 1014 1034(f3) 1047(f3) 1083(an8)	243(f3) 272(f3) 352(f1) 361(f1) 402 466(f1) 514(f1) 527(f1) 573(f1) 593(an6) 641(an10) 654(an10) 747(f2) 781(f2) 824(f2) 835(f2) 888(f3) 906(f3) 921(f3) 937 } (B5) 962 } 982 } (B1) 1014 1034(f3) 1047(f3) 1083(an8)	237(f2) 260 } (B2) 279 } 310(f2) 340(f1) 392(f1) 402 466(f1) 514(f1) 527(f1) 573(f1) 593(an6) 624(an10) 641(an10) 654(an10) 747(f2) 781(f2) 824(f2) 835(f2) 888(f3) 906(f3) 921(f3) 934(f2) 942(f1) 957(f3) 981(f2) 1019(an3)	234(1) 260(1) 315(1) 345(1) 387(2b) 402 466(f1) 514(f1) 527(f1) 578(f3) 598(f5) 624(an10) 641(an10) 655(f3) 732(f2) 798(f1) 855(f3) 870(f3) 898(f3) 921(f3) 934(f2) 942(f1) 957(f3) 981(f2) 1019(an3)	223 } 243 } (B2) 262(f2) 330(f1) 340 375(B1) 387 } (B1) 416 } 518(f2) 527(f2) 577(f1) 598(f5) 655(an10) 749(f2) 786(f2) 823(f3) 841(f3) 875(f4) 899(f3) 918(an4) 938(f5) 957(f4) 973 } (B4) 988 } 1007(f1) 1024 } (B3) 1050 } 1082(n8)	242(f1) 258(f2) 387(f1) 467(f2) 536(f2) 628(f5) 655(f4) 734(f1) 845 } (B3) 871 } 893(f3) 915(an2) 962 } (B2) 976 } 988 1024(f3) 1065(f4) 1110(f2) 1134(f1) 1168 1249(f)

Camphane and Fenchane.

Bornyl Butyrate	Isobornyl Butyrate	Camphenilone	Camphor				Fenchone		
(4)	(4)	(19)	(12)	(19)	(43)	(94)	(8)	(19)	(43)
170(f1) 211 } (B1) 243 }		205(f5)	139(1)						
272(f1)		287	269(0) 301(2)		254(2b)		217(4) 276(3) 301(3)	221(f2) 280(f3) 300(f4) 330(f1)	202(5b) 260(3) 293(5b)
	391(f1)	371(f3)	392(0)		380(0b) 394(2b)		371(2)	371(f3)	364(2)
			414(0)						418(2)
464(f2)		425(f2) 453(f2)					426(2) 458(2)	424(f3) 454(f3)	445(2)
507(f2)		490(f1)			500(0)				
523(f2)		504(f1)					521(2)	513(f2) 528(f2) 561(f1)	509(0b)
573(f1) 585(f3)	575(f1)	592(f1)	553($\frac{1}{2}$) 596($\frac{1}{2}$)	556(f1)	549(1)				
	624(f3)			612(f1)	595(0)		606(5)	601(n10)	594(2)
652(an6)	652(f2)	650(6n18)	649(5)	652(f8)	645(8)	650(48)		651(n10) 663(n10)	658(2)
		705(f2)	704(f2)	709(f2)	703(2b)		668(5) 724(2)	695(f1) 716(f3)	708(0)
747(f2)							777($\frac{1}{2}$)	776(f1) 827(f5)	771(1) 819(0)
824(f1) 835(f2) 864(f1) 881 } (B2) 902 } 917(f3) 939 } (B4) 959 } 981(f3)	834(f1) 804(f2) 873(f1) 893 (B1) 923 947(f2) 1000(f1)	816(f2) 875(f2)	860(1 $\frac{1}{2}$ d)	859(f3)	852(d)	854(18)	837(4) 889(2)	889(n8)	850(0) 881(4)
		913(f6) 936(f10) 957(f8)	910($\frac{1}{2}$) 931(l) 950(1)		914(2)			923(f5)	927(4)
		997(f4) 1010(f5) 1033(f5)		981(f1)	982(0) 1017(0)			995(f2) 1017(f2)	988(3) 1012(1)
1026 } (B4) 1050 } 1081(an4)	1021(f2) 1048(f1) 1084(f2)		1034(2d)	1038(f1)			1013(1)		
			1094(1d)	1088(f1)	1090(1)		1076(1)	1072(f2)	1066(2)
1111(f2) 1134 } (B1) 1148 }	1110(f1) 1152(f1)	1104(f6) 1132(f6) 1155 } (B4) 1170 } 1183(f5)	1161(1d)	1163(f1)	1147(0)			1110(f6) 1155(f3)	1103(3b) 1150(1)
1191 } (B3) 1206 } 1221 } (B3) 1233 } 1258(f3)		1229(f6)	1194($\frac{1}{2}$) 1218($\frac{1}{2}$) 1244(1)	1200(f2) 1222(f2)	1188(1)			1193(f1) 1219(f1)	
			1245(f2)	1238(1)	1243(0)	1243(3)	1243(3)	1241(f3) 1258(f2)	1241(1)

TABLE VIII

amphane	Camphene	Borneol	Bornyl Formate	Iso-Bornyl Formate	Bornyl Acetate	Iso Bornyl Acetate		Bornyl Propionate	Iso-Bornyl Propionate	
(20)	(20)	(64)	(4)	(4)	(4)	(4)	(54)	(4)	(4)	
98(f1)		1298($\frac{1}{2}$)	1281(f4)	1276(f2)	1276(f2)	1278(f1)	1323(2b)	1284(f3)	1274(f2)	
			1306(f5)	1293(an3)	1304(an4)	1298(f1)		1308(an5)	1295(?)	
			1334(f2)	1315(f3)	1329(f1)	1323(f1)		1334(f2)	1304	
			1377 } (B5)	1367 } (B4)	1360(f1)	1357(f1)		1369(?)	1332 } (B1)	
99 } (B4)	1430 } (B8)	1442(2b)	1395 } (B5)	1392 } (B4)	1373(f2)	1382(f2)	1376(3b)	1386(?)	1360 } (B2)	
			1407 } (B8)		1386(?)				1409	
			1488(f5)	1436(f8)	1406(f1)				1430 } (B4)	
			1474(2b)	1404(f8)	1437 } (B15)	1437(f6)		1438 } (B 6)	1467	
94 }	1672(an10)	1474(2b)	1488(f5)	1491(f3)	1483(f2)	1480(f2)	1440(4bd)	1466 } (B 6)		
			1725(f5)	1725(f3)				1492(?)		
					1739(f3)	1739(f2)		1735(3)	1739(3)	1739(f1)
			2738(0b)							
		2873(1)					1735(3)			
			2922(2)							
			2948(4b)							
			2981(2)							
							1735(3)			
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							1735(3)			

(Contd.)

Bornyl Butyrate	Iso-Bornyl Butyrate	Camphenilone	Camphor				Fenchone		
(4)	(4)	(19)	(12)	(19)	(43)	(84)	(8)	(19)	(43)
1270(f1) 1301(f3)		1290(f4)	1207($\frac{1}{2}$) 1297($\frac{1}{2}$) 1322($\frac{1}{2}$)	1273(f1) 1290(f2) 1323(f2)	1291(0) 1319(0)		1338(1)	1315(f3) 1378(f2)	1265(1) 1310(0) 1334(0)
1329(f1) 1273 } (B1) 1406 }			1418(2)	1417(f3)	1412(1)	1423(0)	1404(1)	1345(f2) 1415(f1)	1582(0b)
1437 } (B10) 1460 }		1439 } (B10) 1469 } 1492(f4)	1448(2 $\frac{1}{2}$ d) 1476(2d)	1443(f4) 1472(f3)	1440(1)		1455(4)	1436 } (B9) 1478 }	1450(5) 1484(2)
1739(f2)		1745(f10)	1734(1 $\frac{1}{2}$ d) 2808(1 $\frac{1}{2}$) 2031(2d) 2970(2d)	1747(f6)	1738(5) 2872(2b) 2946(5bb)	2838(3) 2925(5) 2968(6b)	1731(4) 2874(3) 2961(5)	1745(f8)	1736(3) 2870(5) 2927(1) 2982(1)

HETEROCYCLIC COMPOUNDS.

Part IX. Coumarins from Substituted Resacetophenones and Ethyl Aceto-acetate.

BY R D DESAI AND M EKHLAS

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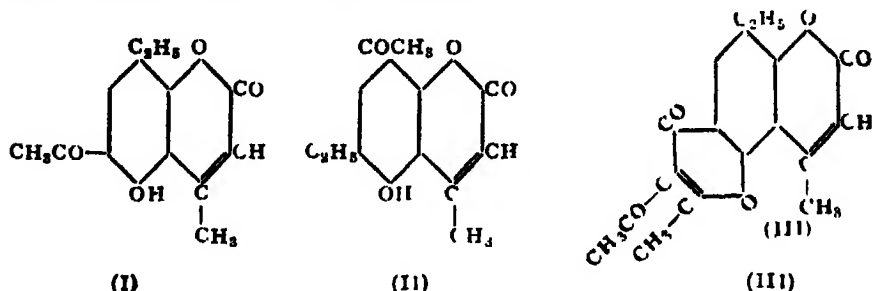
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IN Part IV of this series, Desai and Hamid¹ showed that resacetophenone condensed with acetoacetic ester in the presence of phosphorus oxychloride with the formation of 7-hydroxy-6-acetyl-4-methylcoumarin. The same condensation has been shown to take an entirely different course in the presence of anhydrous aluminium chloride by Sethna, Shah and Shah² with the formation of 5-hydroxy-6-acetyl-4-methylcoumarin, which has now been detected by us in small amounts in the POCl_3 method. As these types of coumarins are important intermediate products for the synthesis of furo- α - and γ -pyrones, and coumarino- α - and γ -pyrones, some of which occur in nature, it was thought desirable to ascertain the influence of constitutional factors on the course of this condensation. (1) 5-Ethylresacetophenone, (2) Orcacetophenone, (3) Gallacetophenone, (4) Respropiofenone, (5) Resbutyrophenone, (6) Resbenzophenone or 4-benzoylresorcinol, (7) 5-Bromoresacetophenone, (8) Methyl- β -resacetophenone carboxylate or Methyl 2 : 4-dihydroxy-5-acetyl benzoate, (9) 2 : 4-diacetylresorcinol, (10) 4 : 6-diacetylresorcinol and (11) Quinacetophenone were condensed with acetoacetic ester in the presence of phosphorus oxychloride with the results described hereunder.

Ethylresacetophenone or 2 : 4-dihydroxy-5-ethylacetophenone gave a coumarin melting at 169° . This might be either 8-ethyl-6-acetyl-5-hydroxy-4-methylcoumarin (I) or 8-acetyl-6-ethyl-5-hydroxy-4-methylcoumarin (II), but as it gave a positive colour reaction with ferric chloride, and underwent the Kostanecki Reaction with the formation of a coumarino- γ -pyrone (III), the contiguous position of OH and $-\text{CO}-\text{CH}_3$ groups was proved beyond doubt. Therefore, the coumarin has got the structure (I). On Clemmensen reduction, it gave 6 : 8-diethyl-5-hydroxy-4-methylcoumarin which was identical with the product obtained from 4 : 6-diethyl resorcinol and acetoacetic ester by Mehta and Shah³. We have also prepared coumarin (I) by the Fries Transformation of 5-acetoxy-8-ethyl-4-methyl coumarin which was obtained from methyl 2 : 4-dihydroxy-5-ethylbenzoate and acetoacetic ester. The

Pechmann Reaction between these two substances would give either 8-ethyl-6-carbomethoxy-5-hydroxy-4-methyl-coumarin or 8-carbomethoxy-6-ethyl-5-hydroxy-4-methyl-coumarin, but the former structure was more probable owing to strong colour reaction with ferric chloride. Hydrolysis of this coumarin ester, followed by decarboxylation, gave 8-ethyl-5-hydroxy-4-methylcoumarin, which has been recently described by Sethna and Shah³ and when its acetyl derivative was heated with aluminum chloride, the coumarin identical with (I) was obtained



Orcacetophenone or 2,4-dihydroxy-6-methyl-acetophenone gave 5-hydroxy-6-acetyl-4,7-dimethylcoumarin, the identity of which was proved by preparing it by the Fries Transformation of 5-acetoxy-4,7-dimethylcoumarin. A small quantity of 5-hydroxy-4,7-dimethyl coumarin was always found, and this was due to the deacetylation of orcacetophenone to orcinol, and subsequent condensation with acetoacetic ester

Gallacetophenone gave a coumarin melting at 148°, and as it gave a reddish brown coloration with ferric chloride, the acetyl group was intact. It was, therefore, assumed to be 7,8-hydroxy-6-acetyl-4-methylcoumarin, but our attempts to prepare it by the Fries Transformation of 7,8-diacetoxy-4-methylcoumarin gave only 7,8-dihydroxy-4-methylcoumarin

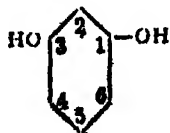
Resorpiophenone gave 6-propionyl-7-hydroxy-4-methylcoumarin, which has been prepared in a very small amount by Limaye and Shenolikar⁴ by the Fries Transformation of 7-propionoxy-4-methylcoumarin. Its constitution was further proved by the preparation of the coumarino- γ -pyrone. As compared with its 6-acetyl analogue, it could be monobrominated with difficulty. Similarly resbutyrophenone gave 7-hydroxy-6-butyryl-4-methylcoumarin as it gave a positive ferric chloride reaction and a coumarino- γ -pyrone. 4-Benzoylresorcinol gave 7-hydroxy-6-benzoyl-4-methylcoumarin which has already been prepared by Limaye⁵ by the Fries Transformation of 7-benzoyloxy-4-methylcoumarin. It gave the coumarino- α -pyrone by the Kostanecki Reaction. Incidentally we have worked out the best method of preparing 4-benzoylresorcinol in quantity by the action of benzoyl chloride

on resorcinol in the presence of anhydrous aluminium chloride, and is much superior to those of Nencki⁸ and Shah and Mehta⁷

5-Bromoresacetophenone, β -methyl-resacetophenone carboxylate, 2·4-diacetyl-resorcinol, and 4·6-diacetylresorcinol did not react under any conditions, while the result with quinaacetophenone was not definite. Owing to close resemblance between α -naphthol and resorcinol in the case of undergoing the Pechmann Reaction with β -ketonic esters, we condensed 4-acetyl- α -naphthol, 4-propionyl- α -naphthol and 4-butyryl- α -naphthol with acetoacetic ester, in the presence of either concentrated sulphuric acid or phosphorus oxychloride, but the acetyl, propionyl and butyryl groups were split off, and all of them gave 4-methyl-1,2- α -naphthapyrone

Thus from the above condensations, one can safely draw the conclusions that the presence of negative substituents like Br, COOCH₃ and COCH₃ hinders the coumarin-condensation of resacetophenone and acetoacetic ester in the presence of POCl₃, while that of the positive groups like CH₃, and C₂H₅ has got no effect at all. Moreover, as the yield of the coumarins from acetoacetic ester, and phenols goes on increasing in the order of 4-benzoyl-resorcinol, resacetophenone, respropiofenone and resbutyrophenone, the hindering effect of the acyl groups is in conformity with their acidic character, the order which is C₆H₅CO > CH₃CO > C₂H₅CO > C₂H₅—CO

From our own work, and the investigations of Clayton,⁸ Chakravarti,⁹ Limaye,¹⁰ Shah¹¹ and their co-workers, plausible explanation on the electronic conceptions can be given for the capacity of phenols and their substitution products to undergo coumarin condensation with open-chain as well as cyclic- β -ketonic esters. The feeble power possessed by ordinary phenol is enhanced by the presence of electron-donating groups in the *meta*-position — e.g., CH₃, OH, OCH₃, NH₂, NHCH₃, N(CH₃)₂, halogens, etc., but depressed and almost annihilated by electron-attracting groups in the same place — e.g., NO₂, SO₃H, COOH, COOME, COCH₃, CN, CHO, etc. Thus resorcinol derives its extraordinary power to undergo coumarin condensation at position 4 (positions 4 and 6 are identical) owing to the election accession from the additional hydroxyl in position (1) which is in the *para*-position to the point of attack, and this activation of position 4 is so great that even the presence of electron-attracting groups at positions 2 or 6 is not sufficient to destroy this power. When position 6 is occupied



by groups which are electron-sinks, the resorcinol derivatives form coumarins with difficulty, while the presence of groups which are electron-sources does not seriously interfere with this property. Moreover, as 2-acetyl resorcin forms coumarins with acetoacetic ester in the presence of concentrated sulphuric acid, but 4-acetylresorcin does not (Limaye, *loc cit*) and 2-nitroresorcin condenses with methylacetoacetic ester, but 4-nitroresorcin does not (Chakravarti and co-workers, *loc cit*), it follows that electron-sinks exercise greater deactivating influence at position 4 than at position 2. With regard to the deactivating effects, the qualitative order is $\text{COCH}_3 > \text{NO}_2 > \text{COOH} > \text{COOCH}_3$ (Compare Desai and Hamid, *loc cit*, also Chakravarti and co-workers). No data is available for CN, CHO and SO_3H groups, but they should exercise greater influence than even the COCH_3 group, and the order should be $\text{CN} > \text{CHO} > \text{SO}_3\text{H}$. We are trying to prepare coumarins from these resorcinol derivatives.

Before concluding, we wish to add a few remarks regarding the condensing agents as they may help the workers in this field. Despite the suggestion of a number of acidic, basic and neutral condensing agents, the best agents are concentrated or 73 per cent sulphuric acid, phosphorus pentoxide, gaseous hydrogen chloride, phosphorus oxychloride, and anhydrous aluminium chloride. One advantage of phosphorus oxychloride is that besides being successful in cases where sulphuric acid is not, it behaves as phosphorus pentoxide in promoting the chromone formation¹². The behaviour of anhydrous aluminium chloride is remarkable in the fact that whereas the other condensing agents promote the formation of 7-hydroxycoumarins from some resorcinol derivatives, this reagent modifies the reaction with the production of 5-hydroxycoumarins which are almost inaccessible by the hitherto known methods (Shah and co-workers, *loc cit*).

Experimental

Condensation of resacetophenone with acetoacetic ester and isolation of 5-hydroxy-6-acetyl-4-methylcoumarin—The original method of Desai and Hamid (*loc cit*) was slightly modified as follows. A mixture of resacetophenone (8 g), acetoacetic ester (6 g), phosphorus oxychloride (2 c.c.) and dry benzene (20 c.c.) was heated on the water-bath for five hours till the evolution of hydrogen chloride ceased. After pouring off the benzene solution, the residue was extracted with two lots of benzene (20 c.c.) and the solvent was removed by distillation from the combined solution. The residue obtained from the benzene solution was recrystallised from alcohol when pure crystals of 7-hydroxy-6-acetyl-4-methylcoumarin melting at 212° were obtained. On Clemmensen reduction, it gave 7-hydroxy-6-ethyl-4-methylcoumarin which

was prepared for comparison from 4-ethylresorcinol, and acetoacetic ester by the usual method (Shah and Samant, *loc cit*) The alcoholic mother-liquor, on concentration, gave the same product in an impure condition The residue left after the removal of the solvent was repeatedly extracted with petrol which, on cooling, deposited small needles melting at 160–162°. Recrystallisation from alcohol raised the m p to 164–165°, and the product was identified as 5-hydroxy-6-acetyl-4-methylcoumarin by comparing it with an authentic specimen prepared by the method of Shah, Sethna and Shah (*loc cit*)

The carboethoxy derivative of 7-hydroxy-6-acetyl-4-methylcoumarin was obtained by cautiously adding ethyl chloroformic ester (2 c c) to the solution of the coumarin (0.5 g) in 5 per cent alkali (10 c c) The insoluble solid was filtered off, and crystallised from dilute alcohol in straw-coloured needles melting at 141° (Found C, 61.8, H, 4.9, $C_{15}H_{14}O_6$ requires C, 62.07, H, 4.8 per cent)

(A) *Condensation of Ethylresacetophenone with acetoacetic ester and synthesis of 5-hydroxy-6-acetyl-8-ethyl-4-methylcoumarin*—A mixture of 2,4-dihydroxy-5-ethylacetophenone (4 g), acetoacetic ester (3 g), phosphorus oxychloride (2 c c) and dry benzene (20 c c) was heated on water-bath under reflux for four hours, and worked up as described before The benzene-soluble fraction was repeatedly extracted with hexane to remove the unreacted ketone The hexane-insoluble portion crystallised from dilute alcohol in colourless needles melting at 169° Its alcoholic solution gave reddish-violet coloration with ferric chloride (Found C, 68.1, H, 5.8, $C_{14}H_{14}O_4$ requires C, 68.3, H, 5.7 per cent) Reduction with amalgamated zinc gave 5-hydroxy-6,8-diethyl-4-methylcoumarin, an authentic specimen of which was prepared for comparison by the method of Mehta and Shah (*loc cit*) The methyl ether of the coumarin (I) was obtained by the usual method, and crystallised from benzene-hexane mixture in needles melting at 173° (Found C, 69.0, H, 6.3, $C_{15}H_{16}O_4$ requires C, 69.2, H, 6.15 per cent)

The acetyl derivative crystallised from dilute alcohol in prismatic needles melting at 149° (Found C, 66.7, H, 5.7, $C_{16}H_{16}O_5$ requires C, 66.6; H, 5.55 per cent)

The semicarbazone crystallised from alcohol in colourless needles unmelted below 285°

The Kostanecki Reaction with 4-methyl-5-hydroxy-6-acetyl-8-ethylcoumarin and synthesis of 4,2'-dimethyl-8-ethyl-3'-acetyl-coumarino-(5,6)- γ -pyrone—A mixture of the above coumarin (1 g), acetic anhydride (8 c c) and anhydrous sodium acetate (2 g) was heated in an oil-bath at 170–180° C for

ten hours. The solid obtained by pouring the mixture into water was collected, and treated with a cold 5 per cent sodium hydroxide solution. The residue crystallised from acetic acid in colourless needles melting at 173° . Its alcoholic solution did not give any colour with aqueous ferric chloride. It dissolved in cold concentrated sulphuric acid and warm sodium hydroxide solution giving yellow solution. (Found: C, 68.9, H, 5.2; $C_{18}H_{16}O_6$ requires C, 69.2, H, 5.1 per cent.)

Synthesis of 4-methyl-5-hydroxy-6-carbomethoxy-8-ethylcoumarin.—A mixture of methyl 2,4-dihydroxy-5-ethyl benzoate (10 g), acetoacetic ester (9 g) and 73 per cent sulphuric acid (50 c.c.) was kept in the refrigerator for 24 hours, and the solid obtained by pouring it over ice was collected. The residue left after treating it with 5 per cent sodium bicarbonate solution, crystallised from alcohol in pale yellowish needles melting at $185-186^{\circ}$ (5.5 g). (Found: C, 63.8, H, 5.4, $C_{14}H_{14}O_6$ requires C, 64.1, H, 5.3 per cent.) The coumarin dissolved in dilute alkali with a yellow colour while its alcoholic solution gave a deep violet colour with ferric chloride. The sodium bicarbonate extract gave, on acidification, the coumarin carboxylic acid (0.2 g.) which crystallised from rectified spirit in needles melting at 240° (effers).

4-Methyl-5-hydroxy-6-carboxy-8-ethylcoumarin was obtained by keeping the solution of the coumarin ester (1 g) in 10 per cent caustic soda (15 c.c.) for three days, and purifying the solid obtained on acidification with hydrochloric acid through sodium bicarbonate. Crystallisation from rectified spirit gave tiny needles melting at 240° (decomp). Its alcoholic solution gave deep violet colour with aqueous ferric chloride. (Found: C, 62.7; H, 5.0, $C_{18}H_{18}O_6$ requires C, 62.9, H, 4.8 per cent.)

4-Methyl-5-hydroxy-8-ethylcoumarin was obtained by heating the above acid at 250° in an oil-bath for one hour. The brown solid was triturated with warm sodium bicarbonate solution, the residue dissolved in 5 per cent caustic soda solution, and the filtered solution acidified with concentrated hydrochloric acid. The solid crystallised from dilute alcohol in colourless needles melting at $211-212^{\circ}$. Its solution in alkali was deep-yellow and non-fluorescent, while its alcoholic solution did not give any colour with ferric chloride. (Found: C, 70.2, H, 5.7, $C_{18}H_{18}O_5$ requires C, 70.6; H, 5.9 per cent.)

The acetyl derivative crystallised from dilute alcohol in small needles melting at $112-113^{\circ}$. (Found: C, 68.1, H, 5.8, $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.7 per cent.)

Synthesis of 4-methyl-5-hydroxy-6-acetyl-8-ethylcoumarin—An intimate mixture of the above acetoxy-coumarin (0.5 g) and anhydrous aluminium

chloride (1 g) was heated in an oil-bath at 140–145° for one hour. The cooled mass was treated with ice-cold hydrochloric acid, and the filtered solid was dissolved in alkali. The solid obtained on acidification was dried and treated with benzene which dissolved a considerable portion. The solution deposited a solid (m.p. 160–164°) which, on recrystallisation from dilute alcohol gave colourless needles melting at 169°, and was identical with the coumarin prepared from 2,4-dihydroxy-5-ethylacetophenone and acetoacetic ester (see before).

(B) *Condensation of orcacetophenone with acetoacetic ester and synthesis of 5-hydroxy-4,7-dimethyl-6-acetylcoumarin*—A mixture of orcacetophenone (2 g), acetoacetic ester (1.6 g), phosphorus oxychloride (1 c.c.) and dry benzene (20 c.c.) was refluxed on water-bath for three hours. The benzene-soluble portion was poured out, and the residue extracted with three lots of benzene (15 c.c. each). After removing benzene, the unreacted phosphorus oxychloride was decomposed by water. After extracting orcacetophenone with water, the residue crystallised from dilute alcohol in needles melting at 178° (0.5 g). (Found C, 66.9, H, 5.0, $C_{18}H_{14}O_4$ requires C, 67.2; H, 5.2 per cent.) Its alcoholic solution gave deep violet coloration with aqueous ferric chloride. The benzene-insoluble portion (1.5 g) crystallised from alcohol in colourless needles melting at 258–259°, and was identical with the authentic specimen of 5-hydroxy-4,7-dimethylcoumarin, prepared from orcinol and acetoacetic ester by the usual method. The acetyl derivative of 5-hydroxy-4,7-dimethylcoumarin crystallised from alcohol in colourless needles melting at 202°.

Fries Transformation of 5-acetoxy-4,7-dimethylcoumarin—An intimate mixture of the above acetyl derivative (1 g) and anhydrous aluminum chloride (2 g) was heated at 140–145° in an oil-bath for one hour. The residue obtained after decomposing the excess of aluminium chloride with ice-cold hydrochloric acid was purified through alkali, and finally crystallised from dilute alcohol when colourless needles melting at 178°, were obtained. It was identical with the coumarin, m.p. 178°, obtained from orcacetophenone and acetoacetic ester.

The acetyl derivative crystallised from dilute alcohol in needles melting at 160° (Found C, 65.8, H, 5.2, $C_{18}H_{14}O_5$ requires C, 65.7, H, 5.1 per cent.)

The semicarbazone crystallised from alcohol in colourless needles unmelted below 280°.

(C) *Condensation of gallacetophenone with acetoacetic ester and synthesis of 4-methyl-6-acetyl-7,8-dihydroxy-coumarin*—A mixture of gallacetophenone

(2 g), acetoacetic ester (2 g), phosphorus oxychloride (1.5 c.c.) and dry benzene (20 c.c.) was refluxed on water-bath for three hours, and the benzene solution poured off. The residue was twice extracted with benzene and the solid recovered after the removal of the solvent was extracted with petrol (b.p. 60–80°). The petrol extract, on cooling, gave a product (m.p. 140–145°) which, on recrystallisation from dilute alcohol, gave colourless needles melting at 148° (yield = 0.5 g). Its alcoholic solution gave a dark reddish-brown colour with aqueous ferric chloride. (Found C, 61.2, H, 4.5, $C_{12}H_{10}O_2$ requires C, 61.5, H, 4.3 per cent.)

(D) *Condensation of respropionophenone with acetoacetic ester and synthesis of 4-methyl-6-propionyl-7-hydroxy-coumarin*—A mixture of respropionophenone (5 g), acetoacetic ester (4 g), phosphorus oxychloride (2 c.c.) and dry benzene (20 c.c.) was refluxed on water-bath for three hours, and the benzene solution poured off. The residue was extracted with three lots of benzene (15 c.c. each), and the solid recovered from the benzene solution. The unchanged ketone was extracted by hot water, and the residue crystallised from methyl alcohol when white needles melting at 227–228° were obtained. (Yield 25 per cent.) It dissolved in alkali giving a red solution while its alcoholic solution gave deep red colour with aqueous ferric chloride. (Found C, 67.0, H, 5.1, Calc. for $C_{13}H_{12}O_4$ C, 67.2, H, 5.2 per cent.)

The acetyl derivative crystallised from dilute alcohol in colourless needles melting at 132°.

The semicarbazone crystallised from alcohol in pale-yellow needles unmelted below 285°.

The carboethoxy derivative crystallised from dilute alcohol in colourless plates melting at 132° (Found C, 62.8, H, 5.4, $C_{14}H_{14}O_6$ requires C, 63.2, H, 5.3 per cent.)

The Kostanecki Reaction with 7-hydroxy-6-propionyl-4-methylcoumarin and synthesis of 4,2',3'-trimethyl-coumarino-(7,6-)-γ-pyrone—A mixture of the above coumarin (1 g), acetic anhydride (10 c.c.) and anhydrous sodium acetate (2 g) was heated at 170–180° for about ten hours. The residue obtained after decomposing the excess of acetic anhydride with water was triturated with cold alkali, and the insoluble portion crystallised from dilute acetic acid when colourless needles unmelted below 270° were obtained. Its alcoholic solution did not give any colour reaction with ferric chloride. (Found C, 70.0, H, 4.8, $C_{16}H_{12}O_4$ requires C, 70.3, H, 4.7 per cent.)

Bromination of 4-methyl-6-propionyl-7-hydroxy-coumarin to 3-bromo-4-methyl-6-propionyl-7-hydroxy-coumarin—To a solution of the coumarin (2 g) in glacial acetic acid (30 c.c.), bromine (1 c.c.) dissolved in glacial acetic acid

(b c c) was gradually added. After the addition of a trace of iodine the mixture was exposed to sunlight for six hours, and heated on water-bath for one hour. The solid obtained by pouring the mixture into water crystallised from acetic acid in colourless needles melting at 140° (Found Br, 25.2, $C_{13}H_{11}O_4Br$ requires Br, 25.7 per cent)

(E) *Condensation of resbutyrophenone with acetoacetic ester and synthesis of 4-methyl-6-butyryl-7-hydroxy-coumarin*—A mixture of resbutyrophenone (3 g), acetoacetic ester (2.5 g), phosphorus oxychloride (2 c c) and dry benzene (20 c c) was refluxed on water-bath for three hours. After the removal of benzene, water was added, and the unreacted ketone was removed by repeated extraction with water. The residue crystallised from methyl alcohol in colourless needles melting at 151° (Yield 30 per cent). The coumarin dissolved in alkali with yellow colour, and its alcoholic solution gave reddish violet coloration with ferric chloride (Found C, 68.1, H, 5.9, $C_{14}H_{14}O_4$ requires C, 68.1, H, 5.7 per cent)

The acetyl derivative crystallised from methyl alcohol in colourless needles melting at 156° (Found C, 66.3, H, 5.7, $C_{16}H_{16}O_5$ requires C, 66.7, H, 5.6 per cent)

Synthesis of 4,2'-dimethyl-3'-ethyl-coumarino-(7,6)- γ -pyrone—A mixture of the coumarin (1 g), acetic anhydride (10 c c) and anhydrous sodium acetate (2 g) was heated at 170 – 175° for ten hours. After decomposing the excess of acetic anhydride, the solid was triturated with alkali, and the residue crystallised from acetic acid when colourless needles melting at 244 – 245° were obtained (Found C, 70.9, H, 5.1, $C_{16}H_{14}O_4$ requires C, 71.1, H, 5.2 per cent)

(F) *Condensation of 4-benzoylresorcinol with acetoacetic ester and synthesis of 4-methyl-6-benzoyl-7-hydroxy-coumarin*—4-Benzoylresorcinol was best prepared as follows—Resorcinol (10 g) and benzoyl chloride (15 g) were alternately added to the solution of anhydrous aluminum chloride (12.5 g) in nitrobenzene (80 c c) and the mixture allowed to remain at the ordinary temperature for 48 hours. Nitrobenzene was steam-distilled off after the decomposition of aluminum chloride with ice-cold hydrochloric acid, and the recovered solid was dissolved in 5 per cent caustic soda, acidified, filtered, and again treated with sodium bicarbonate solution to get rid of benzoic acid. The residue crystallised from hexane in colourless needles melting at 145° (Yield 70 per cent)

Synthesis of 4-methyl-6-benzoyl-7-hydroxy-coumarin—A mixture of 4-benzoylresorcinol (5 g), acetoacetic ester (3 g), phosphorus oxychloride (2 c c) and dry benzene (20 c c) was refluxed on water-bath for three hours

After pouring off the benzene solution, the residue was extracted twice with benzene, and the solid was recovered from the combined extracts. The residue crystallised from methyl alcohol in greenish needles melting at 168–170°, but on recrystallisation from the same solvent, colourless needles melting at 180° were obtained (Yield 10 per cent.) Its alcoholic solution gave a deep red colour with ferric chloride. It could neither be methylated nor acetylated by the usual methods (Found C, 72.5, H, 4.2, Calc. for $C_{17}H_{13}O_4$ C, 72.9, H, 4.3 per cent.)

The semicarbazone crystallised from methyl alcohol in needles melting at 240°

Kostanecki Reaction with 4-methyl-6-benzoyl-7-hydroxy-coumarin and synthesis of 4-methyl-4'-phenyl-coumarino-(7,6)- α -pyrone—A mixture of the coumarin (1 g), acetic anhydride (10 c.c.) and anhydrous sodium acetate (2 g) was heated at 170–175° for ten hours. The residue obtained after decomposing the acetic anhydride was triturated with alkali, and the insoluble portion crystallised from alcohol when the coumarino- α -pyrone was obtained in colourless needles melting at 255°. Its alcoholic solution did not give any coloration with ferric chloride (Found C, 74.7, H, 4.1, $C_{18}H_{13}O_4$ requires C, 75.0, H, 3.9 per cent.)

(G) *Attempted condensations of 4-acetyl- α -naphthol and 5-bromo-resacetophenone with acetoacetic ester*—A mixture of 4-acetyl- α -naphthol (2 g), acetoacetic ester (1.5 g), phosphorus oxychloride (1 c.c.) and dry benzene (10 c.c.) was refluxed for two hours. After the removal of benzene, the residue crystallised from dilute alcohol in colourless needles melting at 173°. The same coumarin was obtained by using concentrated sulphuric acid. 4-Propionyl- α -naphthol, as well as 4-butyryl- α -naphthol gave the same coumarin melting at 173°. This was identified as 4-methyl- α -naphthapyrone. During the course of unsuccessful experiments of condensing 5-bromo-resacetophenone, the following compounds which are new were prepared

3 or 5-Bromoresacetophenone was prepared by gradually adding bromine (2 c.c.) dissolved in glacial acetic acid (10 c.c.) to a solution of resacetophenone (5 g) in glacial acetic acid (25 c.c.), and pouring the mixture into water after keeping it at ordinary temperature for 24 hours. The solid melted at 155°, but recrystallisation from dilute alcohol gave needles melting at 167°. A small quantity of the dibromo-derivative melting at 173–74° was obtained (Found. Br, 34.8, $C_8H_5O_2Br$ requires Br, 34.6 per cent.) It was recovered unchanged on boiling with alkali.

The dimethyl ether was prepared by repeatedly shaking the alkaline solution (0.5 g in 5 c.c. of 10 per cent. NaOH) with dimethylsulphate

(1.5 cc), and crystallised from dilute alcohol in fine, colourless needles melting at 146° . Its alcoholic solution did not give any colour with ferric chloride (Found Br, 30.6, $C_{10}H_{11}O_2Br$ requires Br, 30.9 per cent)

The diacetyl derivative was obtained by heating a mixture of the bromo-ketone (0.5 g), acetic anhydride (5 cc) and anhydrous sodium acetate (1 g.) for three hours. The residue obtained after decomposing the excess of acetic anhydride with water was triturated with alkali and the insoluble solid crystallised from methyl alcohol when straw-coloured needles melting at $161-162^{\circ}$ were obtained (Found Br, 25.7, $C_{12}H_{11}O_5Br$ requires Br, 25.4 per cent)

We are grateful to Dr R. C. Shah for his much useful criticism

Summary

The condensation of acetoacetic ester with substituted resacetophenones in the presence of phosphorus oxychloride has been studied. Ethylresacetophenone, oracetophenone, respropiofenone, resbutyrophenone, 4-benzoyl-resorcinol, and gallacetophenone underwent the desired condensations giving the derivatives of 7-hydroxy-4-methylcoumarins. Negative results were obtained with bromoresacetophenone, methyl, β -resacetophenone carboxylate, 2,4-diacetylresorcinol, 4,6-diacetylresorcinol, 4-acetyl- α -naphthol, 4-propionyl- α -naphthol, and 4-butyryl- α -naphthol. We have also studied the condensation of methyl 2,4-dihydroxy-5-ethylbenzoate with acetic ester for the synthesis of 5-hydroxy-8-ethyl-4-methylcoumarin. An explanation on the electronic conception has been offered regarding the capacity of phenols and their substitution products to undergo the Pechmann Reaction.

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